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RESEARCH/RESOURCES MANAGEMENT REPORT SER–91/04

Hydrochemistry

The ~~Hydrogeology~~ of Southern
Cumberland Island, Georgia

KINGS BAY

ENVIRONMENTAL MONITORING PROGRAM
CUMBERLAND ISLAND NATIONAL SEASHORE

Prepared for DEPARTMENT OF THE NAVY
Naval Facilities Engineering Command
Washington, DC

U.S. Department of the Interior National Park Service

THE HYDROGEOCHEMISTRY OF SOUTHERN

CUMBERLAND ISLAND, GEORGIA

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KINGS BAY ENVIRONMENTAL MONITORING PROGRAM REPORT, ~~KBEMP-90/01~~ SER 91/04

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1990

PREFACE

Cumberland Island National Seashore was established in 1972 to preserve the scenic, scientific, and historical values of the largest and most southerly island along the coast of Georgia. It is well known for its marine turtles, abundant shorebirds, dune fields, maritime forests, fishing, marshes, tidal creeks and flats, and historic structures. The St. Marys Inlet, at the border between Florida and Georgia, is a federally-maintained entrance channel to the Intracoastal Waterway, ports at Fernandina, Florida, and St. Marys, Georgia, and the U.S. Naval Submarine Base at Kings Bay, Georgia. Construction of coastal engineering works and channel dredging over the past 100 years have had noticeable effects on the St. Marys Entrance, Cumberland Island, Georgia, and Amelia Island, Florida. In the early 1960s, Kings Bay was selected as the Navy's home port for Poseidon-class submarines. In the mid-1970s Kings Bay was selected to home port the Navy's new class of Trident submarines. In upgrading the Kings Bay base for the larger Trident submarines, it was necessary to deepen, widen, and lengthen the entrance channel to Kings Bay. The 5-year, Kings Bay Environmental Research Program was conceived in 1986 by the U.S. Departments of the Interior and the Navy. The Navy-funded Program focuses on evaluating the potential effects on the natural resources of Cumberland Island and vicinity of the deepening of the Kings Bay ship channel from 42 ft (12.7 m) to 51 ft (15.5 m). The channel is almost 22 miles (35.2 km) long and required the removal of approximately 35 million cubic yards (26.8 million cu m) of dredged material. The potential biophysical effects of dredging are being evaluated by the National Park Service through a series of biological and geological research projects. The Department of the Navy, through the U.S. Army Corps of Engineers, is monitoring the physical aspects of the ocean shoreline of Cumberland and Amelia Islands and the Cumberland Sound estuary. Technical direction and guidance during the study were provided by Dr. Albert Greene, Jr., National Park Service (NPS); Dr. Thomas J. Peeling, Naval Facilities Engineering Command (NAVFAC); John Headland, NAVFAC; Darryll Molzan, NAVFAC; Dr. Robert Dean, University of Florida, Gainesville (NPS); Dr. Stephen Cofer-Shabica (NPS); and the late Dr. William Odum, University of Virginia, Charlottesville (NPS).

The ultimate goal of this research is to document the potential for short- and long-term changes on the resources of Cumberland Island and Cumberland Sound estuary related to channel dredging. The work described in this report is one of a series of National Park Service studies directed towards this goal.

Stephen Cofer-Shabica

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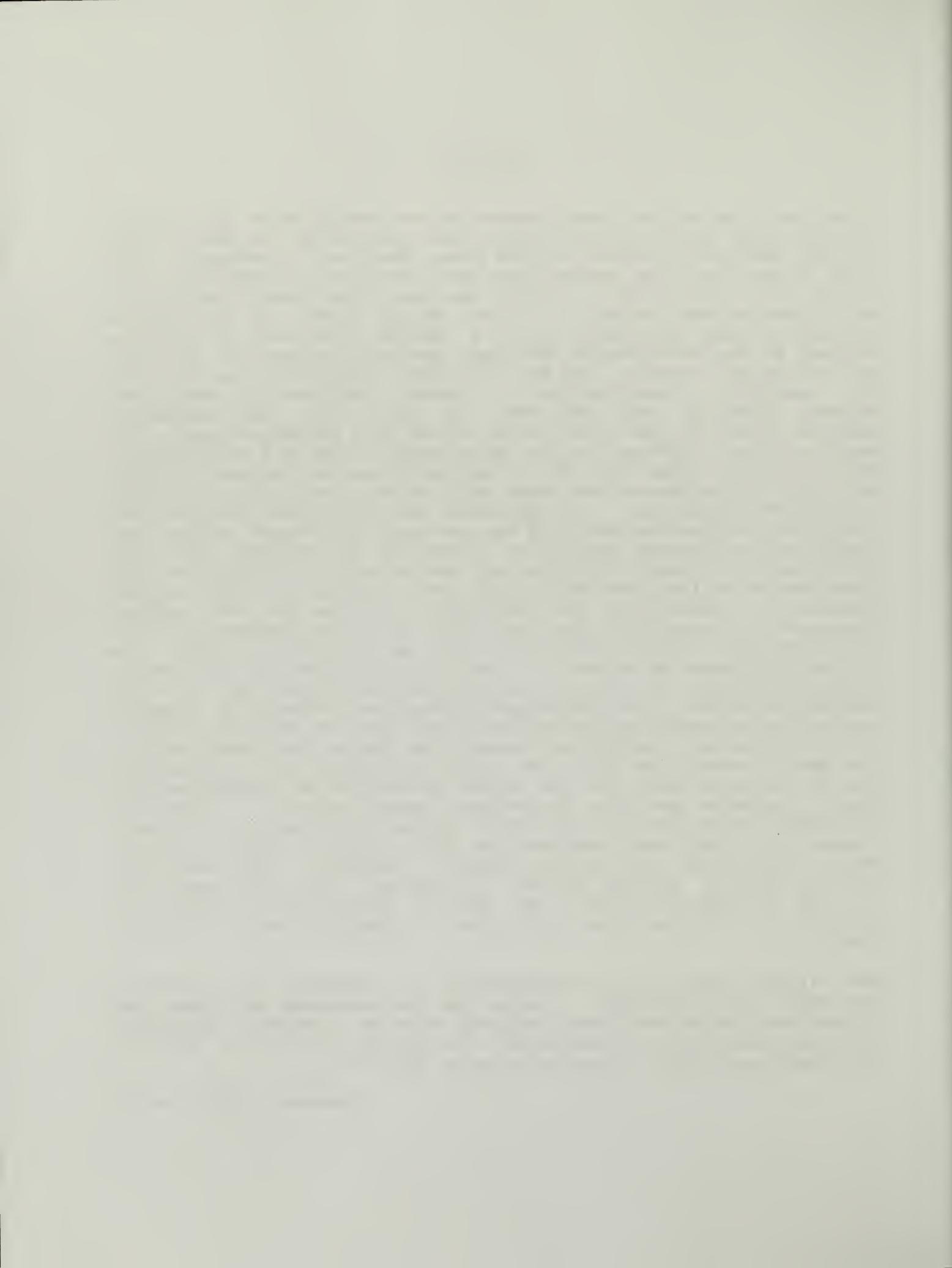
ABSTRACT

The aqueous geochemistry of three aquifers on the southern end
of Cumberland Island, Georgia, was investigated. These aquifers-
--the surficial, the confined Pliocene-Miocene, and a confined
Miocene sand aquifer---were composed of siliceous sand,
fossiliferous dolomite, and calcareous sand, respectively. The
aquifers were monitored by 10 wells that were drilled in two
clusters of three wells and one cluster of four wells. Two of
the clusters were located on the southern coast of the island,
and the third cluster was located northward and inland of these.
The wells were sampled in July and December for seasonal
comparison.

The geochemistry of the surficial aquifer showed seasonal and
geographic variation. The groundwater in the surficial aquifer
varied from sodium-chloride to calcium-bicarbonate, depending on
the location. Seasonal variation was most apparent in the
surficial aquifer at site 1, where the water type changed from
chloride dominant (with no dominant cation) in July to
calcium-bicarbonate in December, most probably as a result of
recharge from rainfall. The geochemistry of the confined
aquifers showed little or no seasonal variation.

The zone of dispersion associated with the freshwater-
saltwater interface was encountered in the Pliocene-Miocene
aquifer and the Miocene sand aquifer, but was not encountered in
the surficial aquifer. The zone of dispersion resulted from
mixing of fresh carbonate groundwater with seawater. This

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mixture initially became undersaturated with respect to calcite. Calcium carbonate in the aquifer matrix dissolved such that the groundwater was supersaturated with respect to calcite. Similarly, the groundwater was supersaturated with respect to dolomite. However, neither dolomite precipitation nor calcite precipitation was indicated by the calcium, magnesium, or bicarbonate ions. Precipitation would decrease these ion concentrations below the concentrations resulting from simple, two-end-member mixing. However, the concentrations of calcium and bicarbonate ion concentrations were much greater than concentrations predicted by simple mixing, and the magnesium concentrations were very similar to concentrations predicted by simple mixing. Therefore, the precipitation of calcite and dolomite must have been kinetically inhibited. Thus, the dolomite present in the Pliocene-Miocene aquifer mixing zone must have been deposited prior to present day.

The sodium-chloride water in the high saline (67 to 88% seawater) region of the zones of diffusion in the Pliocene-Miocene aquifer and Miocene sand aquifer resulted from mixing of two-end members: calcium-bicarbonate groundwater and seawater. Calcium-carbonate dissolution and sulfate reduction also had an effect on the composition of the groundwater. The freshwater region of the zone of dispersion (3 to 5% seawater) was characterized by calcium-chloride water type that probably resulted from freshwater-seawater mixing, calcium-carbonate dissolution, and reverse-ion exchange.

Groundwater samples from the Pliocene-Miocene aquifer at each site were age-dated using the carbon-14 benzene method. The results indicated that modern seawater mixed with 8,000-year-old fresh groundwater in the zone of dispersion.

The zone of dispersion in the Pliocene-Miocene aquifer has intruded farther inland than the zone of dispersion in the Miocene sand aquifer. This may be the result of higher hydraulic conductivity in the Pliocene-Miocene aquifer, greater natural exposure of the aquifer to the ocean, exposure of the Pliocene-Miocene aquifer by dredging, or a combination of these three.

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INTRODUCTION

The work presented here is part of a larger project in which the objective is to determine what effect the dredging of navigation channels in Cumberland Sound will have on the groundwater resources of Cumberland Island, Georgia. The dredging of navigation channels to the south and west of Cumberland Island may have exposed the confined Pliocene-Miocene aquifer to seawater, and thus increased the possibility of saltwater intrusion. The project will evaluate the hydrology of the southern end of Cumberland Island to provide base-line data for the long-term study of the changes in the flow system that may be caused by the dredging. The purpose of this report is to evaluate the hydrogeochemistry of the surficial, Pliocene-Miocene, and Miocene sand aquifers on the southern end of Cumberland Island.

STUDY AREA

The study area is approximately 9 square miles (23.3 km^2), and encompasses the southernmost 3 miles (4.8 km) of Cumberland Island, as well as the areas of Cumberland Sound to the south and southwest of the island which are being dredged for navigational purposes (Figure 1). The island is a National Seashore and is protected from development by Congressional legislation. The only public access to the island is by ferry, and the number of visitors and campers is limited by the National Park Service. Cumberland Island is approximately 16 miles (25.7 km) long and 3
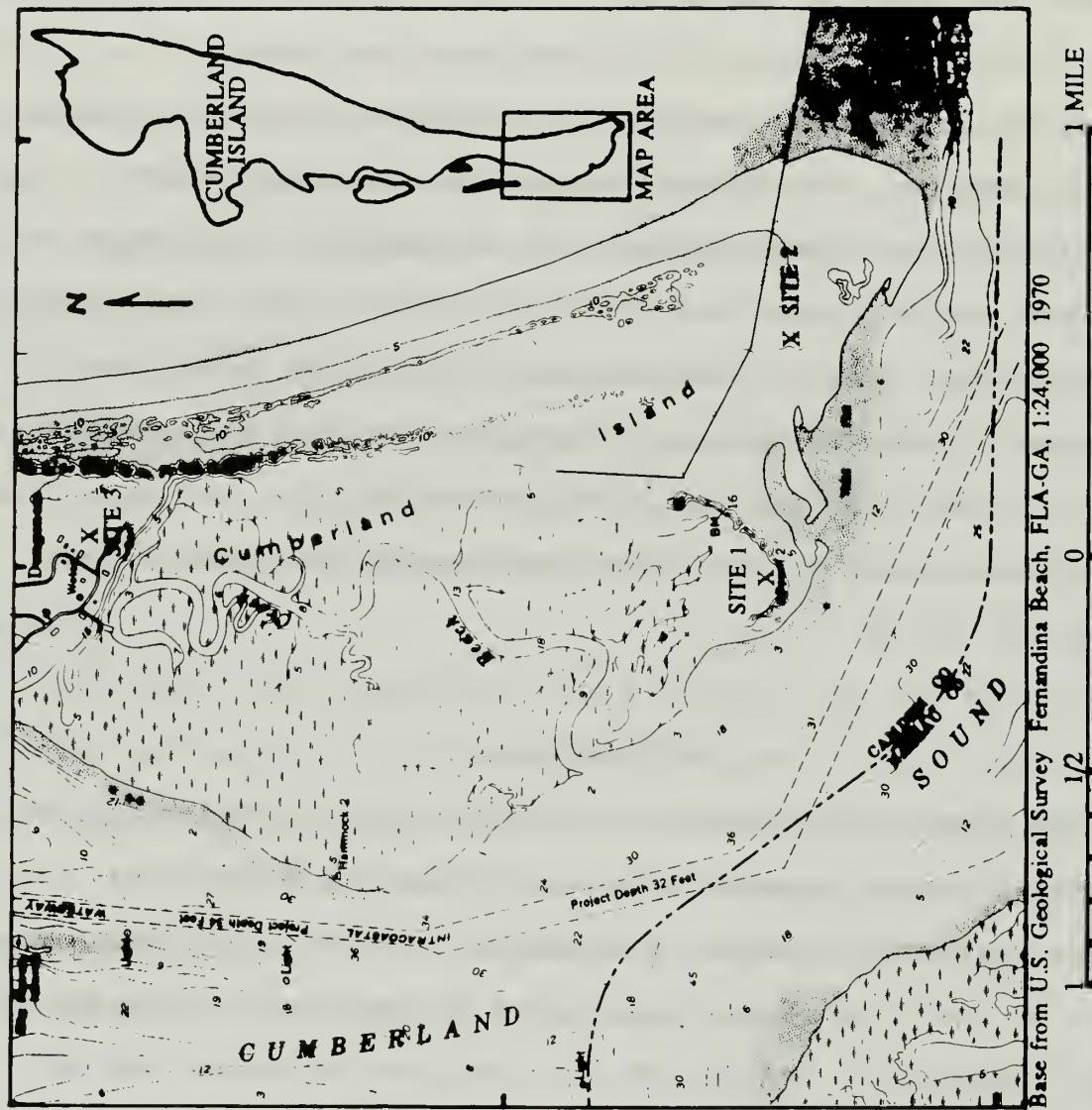
Figure 1. - Map of Study Area and Well Site Location

miles (4.8 km) wide (at its widest). Located in Camden County,
Georgia, it is the largest and southern most of Georgia's barrier
islands. Topography on the island is basically flat and low
lying, with sand dunes providing maximum relief.

OBJECTIVES

This report examines the major ion chemistry of the surficial, Pliocene-Miocene, and Miocene sand aquifers of the southern end of Cumberland Island (Figure 2). The hydrogeochemical evolution of the groundwater of southern Cumberland Island is presented in terms of fluid/mineral equilibria, aquifer lithology and flow systems, biogeochemical processes, and seasonal variation.

PREVIOUS WORK

Barrier Island Hydrogeology

The hydrogeology and geochemistry of barrier islands have been the subject of several studies (e.g., Harris, 1967; Fetter, 1972; Motz, 1982; Boylan, 1986; Vacher, 1988a,b). As explained in the following paragraphs, some of this information may be applicable to Cumberland Island.

The surficial aquifer of a barrier island is composed of a freshwater lens that is recharged by precipitation and seepage from lakes and streams. If the surficial aquifer is of sufficient thickness and is homogeneous, then, according to the Ghyben-Herzberg principal, under hydrostatic conditions the lens will extend 40 feet below mean sea level (MSL) for each foot of head above MSL. Saltwater surrounds this freshwater lens in the unconfined aquifer. If the island is heterogeneous, then the Ghyben-Herzberg lens may not occur. If the surficial aquifer is homogeneous, but underlain by a confining bed at a shallow depth,

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Figure 2. - Generalized Hydrogeologic Column of Cumberland Island

LS = 0	
	SURFICIAL AQUIFER
-30	
	CONFINING BED
-60	
	PLIOCENE-MIOCENE AQUIFER
-94	
	CONFINING BED
-136	
	MIOCENE SAND AQUIFER
-146	
	CONFINING BEDS AND AQUIFERS OF THE
	CHARLTON AND HAWTHORN FORMATIONS
-530	
	UPPER FLORIDAN AQUIFER
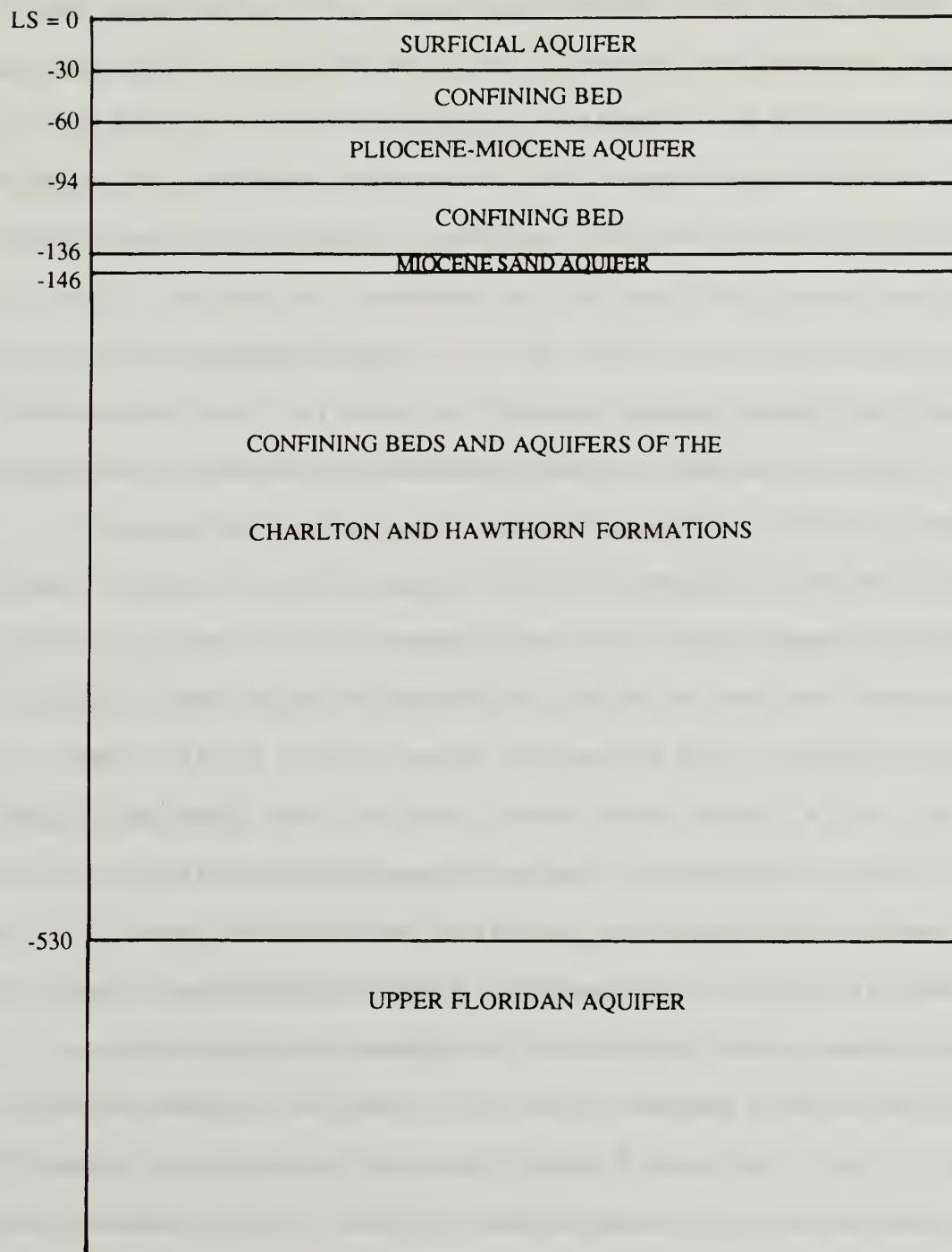
then the freshwater lens will rest on top of the confining bed(Harris, 1967). Assuming the confining bed is truly confining, the freshwater lens will not extend below this layer. Harris (1967), in a study of another heterogeneous barrier island, Hatteras Island, North Carolina, determined that the freshwater lens of the surficial aquifer can lay on top of a clay confining bed. This situation may be similar to Cumberland Island. On Hatteras Island, saltwater lies beneath the confining layer, which is 130 feet (39.6 m) deep. Since the freshwater head in the unconfined aquifer on Hatteras Island is 8 feet (2.4 m), the Ghyben-Herzberg ratio of 40:1 would indicate a freshwater-saltwater interface of 320 feet (97.6 m) below MSL. However, the clay confining layer prevented the freshwater from extending below 130 feet (39.6 m). Thus, the freshwater-saltwater interface occurred at 130 feet (39.6 m) rather than the predicted 320 feet (97.6 m). Freshwater flow in the unconfined heterogeneous aquifer of Hatteras Island flushed the original saltwater from the more permeable zones (yield greater than 5 gpm [19.2 lpm]) at a faster rate than from the less permeable zones (Harris, 1967). The result was a freshwater-saltwater stratification corresponding to relative permeability.

Theoretically, on a homogeneous, isotropic barrier island, the only freshwater would come from the Ghyben-Herzberg lens; however, Cumberland Island, like other barrier islands such as Hatteras Island, NC; Long Island, NY; and North Padre Island, TX, is composed of heterogeneous layers (Harris, 1967; Fetter, 1972;

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McLemore et al., 1981; and Boylan, 1986, respectively). On
Cumberland Island, these stratified layers form an unconfined
surficial aquifer and a series of underlying confined freshwater
aquifers. The confined aquifers of the island outcrop on the
mainland, where they are recharged (McLemore et al., 1981). The
surficial aquifer is recharged over the land surface of the
island by precipitation, seepage from lakes and ponds, and
probably some seawater, depending on the location of the
freshwater-saltwater interface beneath the island.

Barrier Island Geochemistry

The geochemistry of barrier islands, other than the
delineation of the freshwater-saltwater interface, has rarely
been studied. The little geochemical data that are available
come from reports that focused upon the geology or hydrogeology
of barrier islands. One example of this type is the study of
North Padre Island (Boylan, 1986).

Cumberland Island

Cumberland Island has been the object of only one geological
study (McLemore et al., 1981). The resulting report gave a
generalized description of the geology, stratigraphy, hydrology,
and paleontology of the island. It also included geochemical
analyses of the Pliocene-Miocene and Floridan aquifer systems and
lithologic descriptions of several borehole cores.

In coastal Georgia, the Floridan aquifer system is more

heavily utilized than the overlying aquifers, and, as a result, has been the subject of numerous reports and investigations by federal and state agencies, as well as private industry. Unfortunately, most of these reports make no mention of Cumberland Island or the aquifers that lie stratigraphically above the Floridan aquifer system. Some regional studies of the Floridan aquifer system have measured the hydraulic head of Upper Floridan aquifer wells on Cumberland Island (McCallie, 1898; Warren, 1944), while others provide geochemical information pertaining to the Upper Floridan aquifer (Leve, 1966; Stringfield, 1966). These reports are regional studies that cover the coastal area near Cumberland Island. A recent regional report included limited geochemical data from four Cumberland Island wells that were completed within the Upper Floridan aquifer, as well as a lithologic core description of a Cumberland Island Upper Floridan well (Clarke et al, 1990).

Several regional groundwater studies have examined the shallow (surficial, Pliocene-Miocene, and Miocene sand) aquifers as all or part of their report. Most of these examined the hydrogeology and/or geochemistry of coastal Georgia and Florida, without directly studying Cumberland Island. Grantham and Stokes (1976) published water-quality data from several wells in mainland Camden County, GA. A report on the groundwater in eastern Nassau County, FL and southeastern Camden County included geochemical data for 13 wells in the surficial aquifer on the coastal mainland (Brown, 1984). Brown's report, however, recognized only

the surficial and upper Floridan aquifers, making comparison of most of the geochemical data from Cumberland Island difficult. Thus, this report represents the first attempt to synthesize the hydrogeochemistry of Cumberland Island, GA.

BACKGROUND

The following sections on carbonate geochemistry, the freshwater-saltwater interface, carbon dioxide in groundwater, sulfate reduction, and reverse ion exchange are presented as general discussions of the processes occurring on Cumberland Island. These discussions are not specific to Cumberland Island, but are necessary for the understanding of the hydrochemical processes thought to occur within the study area.

Carbonate Geochemistry in Mixing Zones

The hydrogeology and hydrogeochemistry of an island can be separated into four major environments: 1) the unsaturated (or vadose) zone, 2) the freshwater saturated zone, 3) the zone of dispersion (or mixing zone of freshwater and saltwater), and 4) the saltwater (or marine phreatic zone) (Longman, 1982). The freshwater saturated zone consists of both unconfined and confined aquifers that are saturated with freshwater (<1000 mg/L TDS) and have 0% seawater content. The zone of dispersion is that area saturated with a mixture of freshwater and saltwater varying in concentration from 0 to 100% seawater. This zone is located between the freshwater saturated zone and the saltwater

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saturated zone. The saltwater zone is that region of sediment saturated by 100% seawater. The extent and location of these zones is not static, but fluctuates in response to various pressures and changes. For example, in a geographic region with wet and dry seasons, the size of the freshwater zone expands during the wet season due to the increased recharge, and shrinks during the dry season due to lower recharge. This section will concentrate on the geochemistry of calcite and dolomite in the mixing zone environment.

Calcite and Aragonite Stability in Mixed Water

As seawater intrudes into a confined freshwater aquifer, it usually forms a zone of dispersion with the freshwater. The freshwater and seawater mix within the zone of dispersion as a result of convection and molecular diffusion (Cooper, 1959). When two-end-member waters such as freshwater and seawater are conservatively mixed, the concentrations in the solution are volume-weighted averages of the original end-member waters. However, because individual ion activity coefficients vary nonlinearly with changes in ionic strength, the thermodynamic activities of the ionic species that control mineral-water reactions in the mixed solution are not linear functions of mixing (Sanford and Konikow, 1989b). In other words, two solutions of different ionic strengths, such as freshwater and seawater, that are both saturated with respect to any given mineral, such as calcite, can mix to create a solution which is

either undersaturated or supersaturated with respect to that mineral (Sanford and Konikow, 1989a,b). Similarly, undersaturated waters have been mixed to produce supersaturated mixtures, and supersaturated waters have been mixed to produce undersaturated mixtures (Runnels, 1969; Wigley and Plummer, 1976). Computer-simulated mixtures of calcium-carbonate groundwater and seawater (both saturated with respect to calcite) showed that the resultant undersaturated, saturated, or supersaturated solution was a function of ionic strength, partial pressure of carbon dioxide (pCO_2), temperature, degree of calcite saturation, and the pH of end-member solutions before mixing (Plummer, 1975). Differences in the ionic strength, pH, pCO_2, temperature, and degree of calcite saturation of the end members have been shown to result in mixtures undersaturated with respect to calcite. These factors have been shown to be cumulative on lowering the saturation state of the fluid with respect to calcite (Wigley and Plummer, 1976). Mixtures with a high $pCO2$, a high ionic strength, a low pH, and a low temperature achieve the greatest undersaturation with respect to calcite, and can, therefore, dissolve the greatest amount of calcite (Plummer, 1975; Sanford and Konikow, 1989b).

Plummer (1975) demonstrated, using computer modeling, that certain mixtures (less than 10% seawater by volume) of seawater and groundwater were undersaturated with respect to calcite. In mixtures greater than 10%, the degree of undersaturation increased with increasing pCO_2 and decreasing temperature.

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Mixtures that contain a high percentage of seawater and that had a low log pCO_2 (-2.0 to -4.0 atm) were shown to be supersaturated (Plummer, 1975).

The degree of saturation of calcite in the freshwater end-member component also has been shown to have an effect on the mixture. The mixing of undersaturated groundwater with seawater increased the degree of undersaturation within the mixture, while the mixing of supersaturated groundwater with seawater caused undersaturation in some mixtures and supersaturation in others (Plummer, 1975).

Mixed solutions of groundwater and seawater that are undersaturated with respect to calcite have been described as the cause of extensive dissolution in mixing zones of carbonate aquifers such as the Yucatan Peninsula, Mexico (Stoessel et al., 1989). By implication, the dissolution of aragonite occurs in mixing zone waters in which calcite dissolution occurs (Stoessel et al., 1989). Because the solubility of aragonite is higher than calcite, aragonite dissolves slightly faster and more extensively than calcite for a given mixture (Busenberg and Plummer, 1986; Sanford and Konikow, 1989b).

Dolomite Stability in Mixed Water

Dolomites have been reported in numerous studies of freshwater-saltwater mixing zones (Back and Hanshaw, 1970; Hanshaw et al., 1971; Badiozamani, 1973; Randazzo and Bloom, 1985; Stoessell et al., 1989). The formation of dolomite in

mixing zones, and whether it is formed in mixing zones, are the subjects of some contention (Hardie, 1987).

As previously discussed, the mixing of fresh groundwater and seawater to create a mixing zone can result in a solution either undersaturated or supersaturated with respect to dolomite. The nature of the resultant solution is dependent on the pH, ionic strength, temperature, pCO_2, and saturation state of the initial solutions.

In the ocean and in the marine phreatic zone, dolomite does not precipitate even though the Mg/Ca ratio is high and the seawater is supersaturated with respect to dolomite. A logical assumption would be that mixed waters that are supersaturated with respect to dolomite would also fail to precipitate dolomite in zones of diffusion; however, freshwater-seawater mixing zones have been cited as a major environment for dolomitization (Hanshaw et al., 1971). The reasons for this appear to be a combination of factors that commonly occur in mixing zones. Briefly, these involve the Mg/Ca ratio, the dynamic environment, source of Mg, and kinetics. These factors will be discussed subsequently.

Many mixtures of seawater and carbonate groundwater are supersaturated with respect to dolomite and undersaturated with respect to calcite. This situation has the thermodynamic potential for dolomitization by dissolution of calcite and replacement with dolomite (Hanshaw et al., 1971). The "Dorag" model of dolomitization (Badiozamani, 1973) predicted

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dolomitization by replacement of limestone with dolomite in mixed water compositions of 5 to 30% seawater. Stoessel et al. (1989) showed that certain mixed water compositions of 5 to 90% seawater have the potential for replacement of limestone by dolomite in one mixing zone. Not all freshwater-seawater mixtures favor replacement of limestone with dolomite, however. For example, Plummer (1975) showed that only certain mixtures of carbonate groundwater and seawater at specific temperature, pCO_2s, pHs, and initial saturations were capable of producing a solution with the potential to replace calcite with dolomite. In short, given the variability of pCO_2, pH, temperature, and ionic strength, there is only a limited range of mixing-zone salinities in which dolomite can replace calcite.

Dolomitization appears to be the result of some or all of these factors: 1) a Mg/Ca ratio greater than 1 to 3; 2) a dynamic environment with sufficient water circulation; 3) kinetics (sufficient time); 4) an unlimited source of magnesium ions; 5) a high CO_3 ion content to overcome the magnesium-dehydration barrier (Hanshaw et al., 1971; Folk and Land, 1975; Hanshaw and Back, 1979).

Mixing zones of seawater and carbonate freshwater often have all of these properties. A mixing zone is a dynamic environment in which constant mixing of freshwater and saltwater occurs. In higher hydraulic conductivity aquifers, tidal influence cyclically moves the location of the zone of dispersion. In such a situation, if dolomitization was occurring, the area being

dolomitized would increase because of the movement of the mixing zone. Because mixing in the zone of dispersion is driven by density convection (Cooper, 1959), seawater is continually supplying the freshwater-saltwater mixture with magnesium ions, which is another important factor in dolomitization. Whether or not the Mg/Ca ratio is greater than 1 to 3 is dependent on the specific content of the mixed groundwater. Another factor, sufficient time for dolomitization, may be available in stable mixing zone environments such as Cumberland Island.

Groundwater with a high carbonate ion content may also be necessary to break down the magnesium-dehydration barrier. The magnesium-dehydration barrier is the strong bond formed between magnesium ions and water molecules in solution. Calcium ions also form this bond, but they are one-half the strength of the magnesium bonds. Carbonate ions apparently posses enough energy to dehydrate the calcium ions and, given sufficient carbonate concentration, they can dehydrate the magnesium ions. Since this ability to dehydrate is proportional to the carbonate ion concentration, dolomite and magnesite do not naturally precipitate in seawater because of the low carbonate ion concentration (Hanshaw and Back, 1979). Hanshaw and Back (1979) theorized that a high carbonate ion concentration in a mixing zone would help overcome the magnesium-dehydration barrier and aid in the formation of dolomite. This information indicates that a highly alkaline, possibly carbonate dominant, environment may be necessary, or at least helpful, in dolomite precipitation.

Hanshaw and Back (1979) gave no indication of the actual concentrations of carbonate ions that were necessary to overcome the magnesium-dehydration barrier effect. Presumably, it is some concentration greater than seawater, and, in theory, the higher the concentration the greater the potential for dolomitization. However, since very few carbonate-dominant (pH>10.33) waters exist in nature, the carbonate concentration may not be a necessary or dominant factor in the formation of dolomite.

Sources of Carbon Dioxide in Groundwater

Rainwater, which is in equilibrium with carbon dioxide in the atmosphere, is a principal source of groundwater recharge. The log pCO_2 of atmospheric carbon dioxide is -3.5 atm. When rainwater enters the soil, the pCO_2 in the water increases to a log pCO_2 of about -2.0 atm (Drever, 1988). This results from root respiration and the decay and oxidation of organic carbon. The concentration of carbon dioxide gas in soils is commonly several hundred times that of carbon dioxide in the atmosphere (Trainer and Heath, 1976). Root respiration expels carbon dioxide into the soil as a product of a reaction within plants that consumes oxygen and carbohydrates. The decay of organic matter into organic carbon is accomplished by microorganisms within the soil. The organic carbon is then oxidized by free oxygen molecules within the soil (Bolin, 1974).

When the CO_2-enriched rainwater enters the saturated zone it may or may not become isolated from the source of CO_2. If the

groundwater becomes isolated from the source of CO_2 (closed system), then any geochemical reactions that involve CO_2 are limited by the isolated initial partial pressure of CO_2. However, if the groundwater is continuously recharged with CO_2-enriched waters (open-system), then these geochemical reactions would not be restricted by a limited supply of CO_2. For example, consider a carbonate aquifer with CO_2-enriched groundwater. Calcium carbonate dissolves according to the reaction:

(1) $CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$.

If the supply of CO_2 in this reaction is limited, then the amount of $CaCO_3$ that can be dissolved by the groundwater is also limited. However, if the CO_2 is recharged, then the dissolution of $CaCO_3$ is not limited by the availability of CO_2 (Drever, 1988).

Groundwater enriched in soil-derived CO_2 can become part of the water in a confined aquifer system, and be continuously recharged with CO_2 long distances from its recharge area. The main aquifer of the Floridan aquifer system has been shown to receive soil-derived CO_2 for significant distances down gradient of its recharge area (Plummer, 1977).

The oxidation of organic carbon is another possible source of CO_2 in groundwater. The equation for the oxidation of organic carbon is:

(2) $CH_2O + O_2 = CO_2 + H_2O$.

The organic carbon is oxidized by the oxygen molecules in aerobic

groundwater, and CO_2 is produced. This production of CO_2 would increase the pCO_2 in the groundwater.

Sulfate Reduction

Sulfate depleted solutions from a zone of dispersion within a coastal aquifer have been reported from Israel (Nadler et al., 1980). Sulfate reduction was reported as the mechanism responsible for the depletion of sulfate from the mixed waters. As will be subsequently discussed, sulfate reduction is a possible reaction in the mixing-zone groundwaters of Cumberland Island.

Sulfate reduction is a reaction caused by the bacteriological breakdown of organic carbon in an anaerobic environment. The reaction is:

$$(3) SO_4^{2-} + 2C_{organic} + 2H_2O = H_2S + 2HCO_3^-.$$
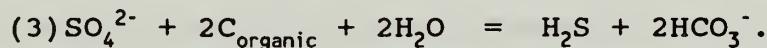
The bacteria use the sulfate to oxidize the organic carbon. Hydrogen sulfide is a by-product of this reaction at pHs below 7, and HS^- is produced at pHs above 7 (Drever, 1988).

Reverse Ion Exchange

Reverse ion exchange has been previously reported in a zone of dispersion within a coastal aquifer by Nadler et al. (1980). Reverse ion exchange is also a process that may affect mixing-zone chemistry in Cumberland Island groundwater.

Reverse ion exchange is a process in which calcium ions in freshwater sediments are exchanged for sodium, potassium, and

magnesium ions in seawater solutions. This exchange occurs when seawater comes into contact with freshwater sediments, such as in freshwater-saltwater mixing zones. The result of reverse ion exchange is increased calcium-ion concentration, and decreased concentrations of sodium; potassium; and magnesium ions. Therefore, Ca/Cl ratios should increase, while Na/Cl, K/Cl, and Mg/Cl ratios should decrease compared to a conservative species such as chloride.

Computer simulation of a freshwater-saltwater mixing zone indicated that sodium ions from saltwater were exchanged for calcium ions from freshwater sediments (Appelo and Willemsen, 1987). Bicarbonate ion concentrations reportedly decreased slightly during the mixing of seawater and freshwater. This decrease has been explained as the precipitation of calcite (Appelo and Willemsen, 1987). The results of these computer simulations indicate that Na/Cl and HCO_3/Cl ratios should be less than seawater, and Ca/Cl ratios should be greater than seawater.

Freshwater-Saltwater Interface

Two different types of interface are possible where saltwater and freshwater meet within an aquifer. The first type is a sharp boundary between the freshwater front and the saltwater front. Groundwater flow does not occur across a sharp interface, and molecular diffusion dominates the mixing of water at the interface (Volker and Rushton, 1982).

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The second possibility for a freshwater-saltwater interface is
a zone of dispersion. The zone of dispersion is the region
within a coastal aquifer in which fresh- and saltwater mix as a
result of dispersion. Dispersion is defined as the result of
density convection and molecular diffusion (Cooper, 1959), or as
the result of mechanical mixing and molecular diffusion (Freeze
and Cherry, 1979). For this paper, mechanical mixing and mixing
by convection will be considered as the same process that
contributes to the creation of the zone of dispersion. As
seawater mixes with freshwater, it becomes less dense and rises
along a seaward path resulting in a circulation pattern. This
circulation is analogous to thermal convection, differing only in
that changes in density are the result of changes in salt
concentration rather than changes in temperature. This
circulation decreases the extent to which the saltwater intrudes
into the aquifer. The salts that become mixed into the
freshwater system are continually carried back toward the ocean
by the flow of freshwater toward the sea (Cooper, 1959). As the
saltwater wedge moves back and forth at the interface within the
aquifer, variations in fluid velocities (i.e., mechanical
dispersion) results in the mixing of fresh and saltwater.
Convection is the dominant process in mixing in aquifers with
high groundwater flow velocities. If the groundwater flow
velocity is low (i.e., less than 1 meter per year), then
diffusion rather than convection becomes the dominant process in
mixing (Appelo and Willemsen, 1987). A transition zone exists

between convection-dominated and diffusion-dominated mixing at low to intermediate (unquantified) groundwater flow velocities in which both processes are important (Freeze and Cherry, 1979).

Each aquifer within a system has a different dispersion coefficient, and determining actual values within real systems has proven difficult (Volker and Rushton, 1982). The dispersion coefficient is defined by the following equation:

(4) $D = av + D*$.

where D is the coefficient of dispersion (L^2/T), a is the dispersivity (L), v is the groundwater flow velocity (L/T), and D* is the molecular diffusion coefficient (L^2/T). In general, the groundwater velocity (v) is the dominant term in the equation. This velocity (v) is a function of the hydraulic conductivity of the aquifer. Higher hydraulic conductivities result in higher flow velocities, that in turn result in higher rates of dispersion and higher dispersion coefficients (Cooper, 1959). The greater the dispersion coefficient, the greater the width of the mixing zone, and the greater the discrepancy between the theoretical sharp interface and the actual zone of dispersion. Dispersivity (a) is a property of the aquifer, and occurs in both longitudinal and lateral directions within an aquifer (Volker and Rushton, 1982). Longitudinal dispersivity occurs in the principal direction of flow, while lateral (or transverse) dispersivity occurs perpendicular to the longitudinal direction (Freeze and Cherry, 1979). Values for longitudinal dispersivity that have been used in previous studies (Volker and

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Rushton, 1982) ranged within the orders of 10^0 to 10^2, while lateral dispersivities are usually 10 to 30% of the longitudinal value. As previously discussed, diffusion is not as important as dispersion (convection) in a dynamic mixing zone, but it becomes the dominant factor if the groundwater flow stops. Therefore, the diffusion coefficient (D*) would not be a dominant factor in determining the dispersion coefficient unless little or no groundwater flow existed.

The width and inland extent of the zone of dispersion are dependent on the amplitude of the tide, the freshwater hydraulic head in the aquifer, the saltwater head, the hydraulic conductivity of the aquifer (Cooper, 1959), the dispersion coefficient of the aquifer, and the freshwater discharge from the aquifer (Volker and Rushton, 1982). The width of the zone is such that the rate of salts being introduced into the aquifer by dispersion is equal to the rate of salts being removed from the aquifer by groundwater flow to the sea (Cooper, 1959).

Within a confined coastal aquifer, the saltwater front moves inland with the rising tide and retreats seaward with the outgoing tide. The greater the amplitude of the tide, the larger the width of the resultant zone of dispersion; and the higher the saltwater head, the farther the inland extent of the zone of dispersion. A high freshwater hydraulic head would tend to retard the inland flow of saltwater, while a lower freshwater hydraulic head would not be as resistant to the inland flow of saltwater. Computer modeling in a previous study (Volker and

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Rushton, 1982) indicated that reducing the freshwater discharge to the zone of dispersion increased the width of the zone of dispersion and moved the zone of dispersion significantly landward. Hydraulic conductivity is another important factor in the inland extent of saltwater flow. The higher the hydraulic conductivity of an aquifer, the farther saltwater will intrude into the aquifer, and the faster the rate of dispersion (Cooper, 1959). As previously stated, the higher the dispersion coefficient of an aquifer, the greater the saltwater intrusion into the aquifer (Volker and Rushton, 1982).

RESEARCH METHODS

Field Methods

A surface geophysical scan was conducted with a Geonics EM 34-3 electromagnetic terrain conductivity meter to aid in the initial determination of the freshwater-saltwater interface. Although this technique did not give exact depths to the saltwater interface, the approximate location was determined by denoting the areas in which the apparent conductivity changed sharply in a short horizontal distance (Stewart, 1982). The variable spacing and dipole capabilities of the EM-34-3 allowed terrain conductivity measurements for various depths at points along several transects of the island. The latitude, longitude, and elevation of each measuring point were surveyed. The conductivity values of each location and depth were plotted on a map to aid in the determination of the most favorable drilling

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sites for the monitoring wells. Three sites were chosen, and ten wells were drilled (Figure 1). During the well drilling, the first borehole (well 1) was continuously split-spoon sampled until hard rock (dolomite) was encountered; it was continuously cored from the top of rock to its finished depth of 146 feet (44.6 m). The core from this well and the cuttings from all other wells were lithologically described. This information was used to determine which aquifers were being drilled, to create stratigraphic cross sections, and to provide lithologic information for interpretation of the geophysical logs.

The deepest borehole at each site was logged with natural gamma, resistivity, and spontaneous potential (SP) geophysical logs (on file with the USGS-WRD, Atlanta, GA). These logs were used in determining the depth of well placement and the interval to be screened and monitored. The logs will also be used in another study to better determine the hydrogeologic framework of the island.

In order to analyze the water quality of the aquifers of Cumberland Island, samples were collected from one existing well, as well as the ten new wells that were drilled on the southern end of the island for use in monitoring changes in the freshwater-saltwater interface. These new well sites were located near the coastline at two locations where the navigation channel is closest to the island. The well sites are in two clusters of three wells and one cluster of four wells (Figure 3). These wells are completed within the surficial, Pliocene-Miocene,

and Miocene sand aquifers (Figure 3).

Water from the wells drilled in the study area was sampled and analyzed for the major constituents. Two sets of water-quality samples were taken from each of the ten wells drilled for this project. The first set of samples was taken during July, 1989, and the second set was taken in December, 1989. During the December sampling event, one existing well was sampled and designated well 11. The alkalinity, water temperature, pH, dissolved oxygen (DO), and specific conductance of the samples was measured in the field.

Before samples were taken, each well was developed by pumping several well-bore volumes from the well. While purging the wells, the groundwater was monitored for specific conductance, pH, and water temperature.

After purging, aquifer waters were sampled with a submersible pump. The pH and temperature were measured by inserting the probe from the pH meter into the discharge hose, and waiting for the readout to stabilize before taking a reading. Inserting the probe into the discharge hose prevented the water from coming in contact with the atmosphere, which would increase the pH value by the outgassing of CO_2. The DO was fixed into solid MnO_2 in the field. Dissolved-oxygen concentrations were then determined using the azide-modified Winkler titration method described by the American Public Health Association (APHA, 1985). Alkalinity was determined in the field by titrating samples with 0.0200 N sulfuric acid.

Figure 3. - Stratigraphy of Well Sites

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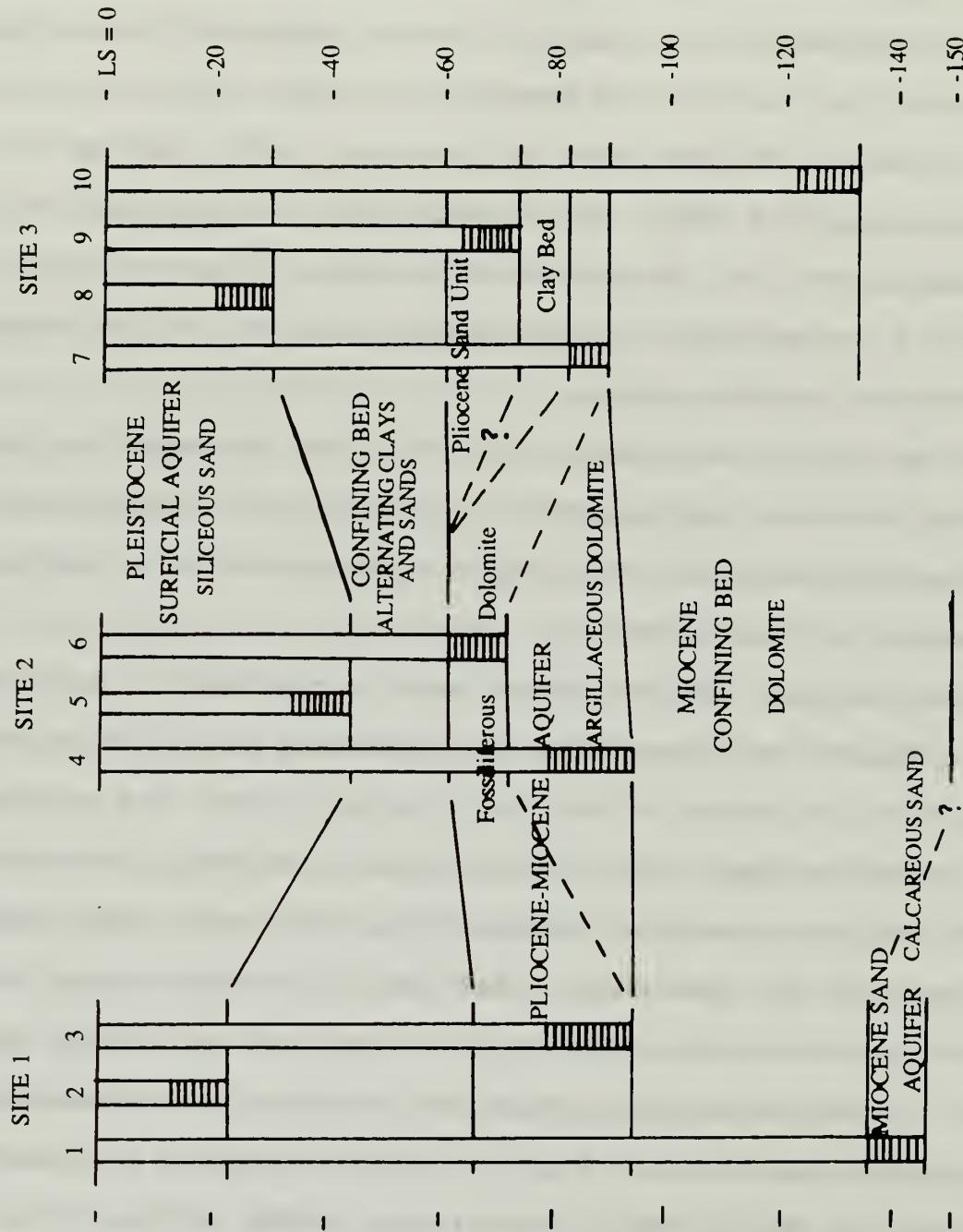
Specific conductance and temperature of the groundwater samples were measured using a HACH DREL/5 specific conductance meter with a temperature compensator. The samples were measured by submersing the probe from the meter into a beaker of water taken from the discharge hose.

Sampling Procedures

The ten wells drilled for this project were developed using a 0.5-horsepower, submersible pump for 4-inch (10-cm) wells. The pump was rated at 8 gpm at a maximum depth of 500 feet (152.4 m). For sampling, the pump was lowered into the well bore to a depth that varied between 2 and 10 feet (0.6 & 3.0 m) from the bottom of the well, and suspended in place with a 0.125-inch (0.3-cm) steel cable. One-inch-diameter (2.5-cm) PVC pipe was used as the discharge pipe from the pump. The pump was powered by a 115-volt, portable gasoline generator.

The wells were developed by pumping and surging the wells. The volume of water removed from each well during development varied from well to well. The factors that affected the volume of water pumped from each well during development included the volume of drilling fluid used in drilling the well, the well-bore volume, the hydrologic properties of the aquifer, the capacity of the pump, the pumping rate, and the time necessary for the field monitored parameters (such as temperature and pH) to stabilize.

During the development of the wells, specific conductance, pH, and temperature readings were taken periodically to monitor these parameters. The wells were pumped until these parameters

stabilized, and the wells were then sampled.

The pH was monitored with a Hach One portable pH meter, and the specific conductance was monitored with a Hach DREL/5 spectrophotometer with conductivity probe. The pH meter, the DREL/5, and a mercury thermometer were used to monitor the temperature.

The specific conductance measurements were made by filling a clean 400-ml Pyrex beaker with water from the pump's discharge pipe and then inserting the conductivity probe from the DREL/5 into the sample. Gently stirring of the water with the probe insured that the sample flowed through the probe, and that an accurate measurement would be recorded. The specific conductance of the sample was then read from the analog scale on the DREL/5. The specific conductance meter was regularly checked against a standard with a conductivity of 506 microsiemens to insure accuracy.

With the DREL/5 in the temperature mode, temperature measurements were made in a manner similar to the specific conductance measurements. The probe was placed in a beaker of sample and gently stirred. The temperature of the sample was then read from the analog scale. The mercury thermometer was also placed in the sample beaker and allowed to equilibrate before the temperature was recorded.

The Hach One pH meter was used to monitor the pH of the samples. Each day before pH measurements were taken, the pH meter was calibrated using the automatic calibration mode with

two standards of known pH. The standards were solutions of 4.00 pH and 7.01 pH. With the meter calibrated, it was placed in the pH mode, and the pH meter electrode was then placed into the water sample. A drop of reference-electrode solution was dispensed through the electrode, and the electrode gently stirred in the sample. When the pH and temperature readings stabilized, they were recorded. The pH meter measured the pH and temperature simultaneously and displayed them digitally on the pH meter display. Temperature was displayed in degrees Celsius to the tenth of a degree, while pH was displayed to the hundredth of a pH unit. In order to check the accuracy of sampling the pH with the electrode in a beaker of sample water, the pH electrode was also placed in the discharge pipe, and the results were recorded.

Alkalinity was also measured. When field conditions permitted, alkalinity titrations were done at the drill site, otherwise they were done in a laboratory the same night that the wells were sampled. When the titrations were done in the field, a clean 400-ml beaker was filled with sample water from the discharge pipe. A 100-ml sample was measured and titrated using 0.0200 N sulfuric acid using the method described by the American Public Health Association (APHA, 1985). The Hach One portable pH meter was used to monitor the pH and temperature during the titrations. When the titration was done in the laboratory, a plastic Nalgene sample bottle was filled to the top and sealed to prevent the outgassing of carbon dioxide. Once in the laboratory, a 100-ml sample was measured and titrated as

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previously described.

After the field-measured parameters had stabilized, the wells were sampled. The groundwater samples were collected by filling plastic (Nalgene brand) bottles at the discharge pipe. After alkalinity measurements were made, the groundwater samples were filtered through 0.45-micron filter membrane using a small electric vacuum pump. The samples were then returned to clean Nalgene bottles for temporary storage until they could be analyzed. The samples to be analyzed for cation concentrations were acidified to a pH of less than 2 immediately after filtration. Nitric acid (6 N) was used for acidification.

Laboratory Methods

Water samples from the July sampling event were analyzed by the author at the Georgia State University laboratory facilities. Three of the ten samples from July were also analyzed as a quality control measure by the U. S. Geological Survey Water Quality Laboratory in Ocala, FL. The USGS also provided unknown samples to the author to be used as a quality control check. All of the samples from the December sampling event were analyzed by the USGS Water Quality Laboratory.

All groundwater samples were filtered through 0.45-micron membrane filter. Samples used for cation concentrations (calcium, magnesium, sodium, and potassium) were preserved at low pH with concentrated nitric acid.

Air-acetylene atomic-absorption spectrophotometry was used in

determining concentrations of calcium, magnesium, sodium, and potassium. Dissolved silica concentrations were determined by the colorimetric molybdosilicate method (APHA, 1985). Sulfate concentrations were determined with the barium-chloride turbimetric method using a HACH DREL/5 spectrophotometer. Chloride concentrations were determined with an ion-specific electrode. Alkalinity of the samples was determined by potentiometric titration using the method described by the APHA (1985). Bicarbonate concentrations were calculated using the WATEQF (Plummer et al., 1976) computer speciation program.

Computer Methods

The WATEQF program was used to model the thermodynamic speciation of inorganic ions and the concentration and activities of ionic complexes in solution for a given water analysis. The WATEQF was also used to calculate the saturation indices and molality ratios of the ions.

HYDROGEOCHEMISTRY OF CUMBERLAND ISLAND

The hydrogeologic system of Cumberland Island consists of four aquifer systems (Figure 2): the surficial, the Pliocene-Miocene, the Miocene sand, and the Floridan aquifer systems. Of these, the first three listed are of concern to this study. The surficial aquifer extends to depths of 45 feet (13.7 m) and overlies the Pleistocene aquiclude. The Pliocene-Miocene aquifer is a carbonate sand and fossiliferous dolomite aquifer that

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exists from depths of 61 to 94 feet (18.6 to 28.7 m) below land surface, and is confined by the overlying Pleistocene aquiclude and an underlying argillaceous dolomite. The Miocene sand aquifers are a set of aquifers that extend from the lower confining unit of the Pliocene-Miocene aquifer (approximately 136 feet (41.5 m) below land surface) to the top of the Floridan aquifer system (approximately 530 feet [161.5 m]; McLemore et al., 1981). These sand aquifers are individual sand layers that are confined by layers of dolomite and/or clay. Beneath these sand aquifers lies the Floridan aquifer system.

Surficial Aquifer

The surficial aquifer of Cumberland Island covers most of the areal extent of the island and is comprised of poorly sorted, fine grained, siliceous Holocene and Pleistocene sands with local trace amounts of epidote and hornblende. The encountered thickness of this bed varied from 23 to 45 feet (7.0 to 13.7 m) (Figure 3), but it reportedly ranges from 9 to 62 feet (2.7 to 18.9 m) (McLemore et al., 1981). At some localities, particularly near the beach, sea shells are present in the sands near the surface. The Pleistocene sands overlie undifferentiated Pleistocene clays that form the Pleistocene aquiclude (McLemore et al., 1981). These clays vary from homogeneous clay to silty and sandy clay in composition and from 13 to 30 feet (4.0 to 9.1 m) in thickness.

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Geochemistry: Previous Work

The geochemistry of the surficial aquifer of Cumberland Island has not previously been examined. Although no previous water quality data were available from the surficial aquifer of Cumberland Island, water quality data from the surficial aquifer of mainland Camden County, GA were reported in Clarke et al. (1990). The data were taken from five wells completed within the surficial aquifer at depths of 12 to 18 feet (3.7 to 5.5 m).

The chemical composition of recharge water is likely an important factor in determining the chemical composition of the surficial aquifer of Cumberland Island. Possible recharge sources include precipitation, leakage from surface lakes, ponds, and streams, and influx from seawater where tides bring seawater inland of the freshwater-saltwater interface. With varying sources of recharge, the geochemical composition of the surficial aquifer varied areally over the island.

Geochemistry of the Surficial Aquifer

The composition of the surficial-aquifer groundwater was different at each of the three sites (Figure 4 and Table 1). The groundwater in the surficial aquifer at site 1 (well 2) was a calcium-bicarbonate type, while sites 2 and 3 (wells 5 & 8, respectively; Figure 1) were sodium-chloride types (Table 2). These different water types are the result of the differences in geographic location and aquifer lithology observed at the three

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FIGURE 4
Comparison of Surficial Aquifer Water Quality during December, 1989

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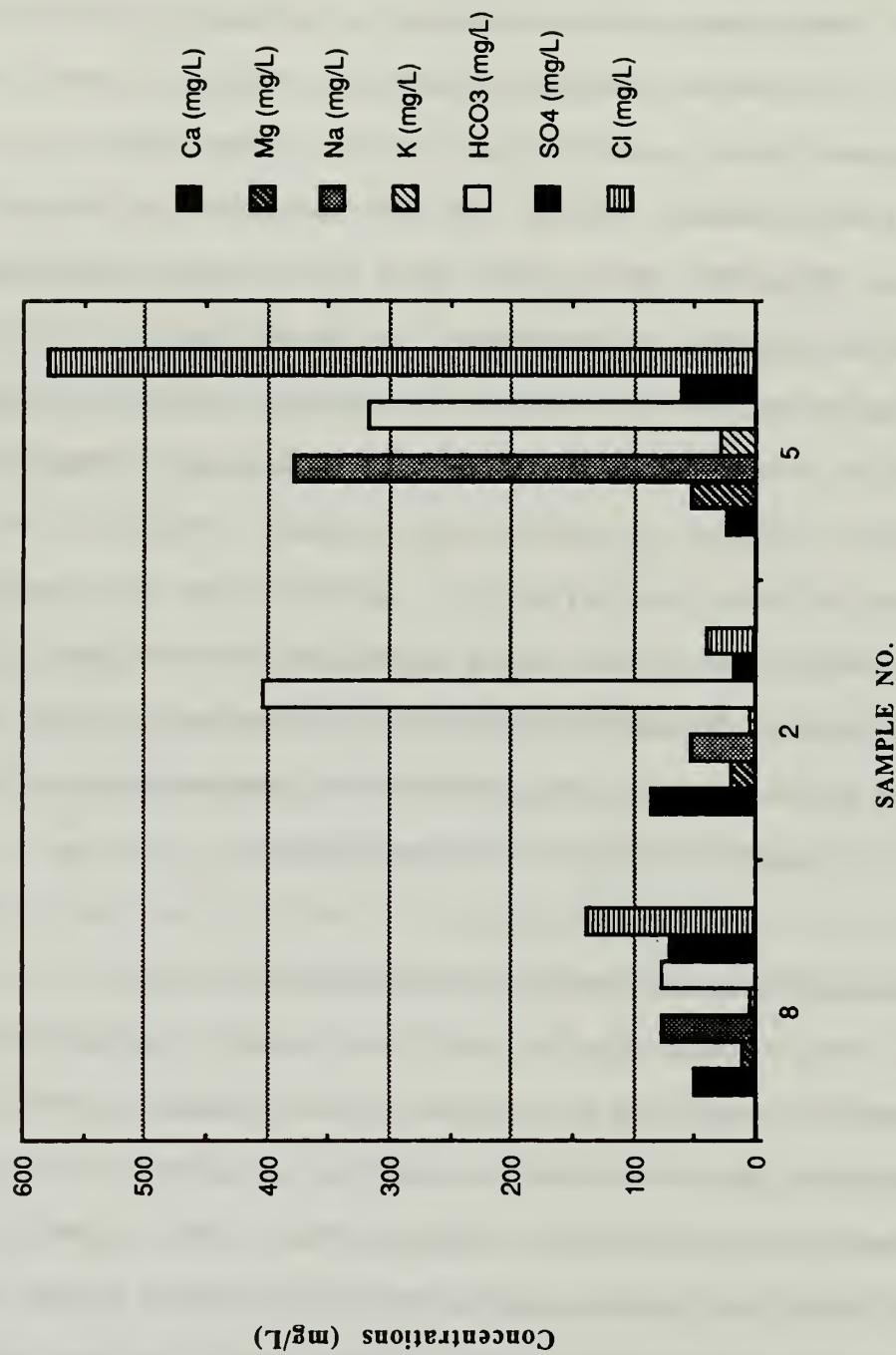
Table 1. Chemical analysis of groundwater samples from Cumberland Island, GA.

sample	pH	Temp (°C)	S.C.	D.O.	Ca	Mg	Na	K	HCO₃	SO₄	Sulfide	Cl	Silica	Flouride	TDS (Calc)	TDS (Res@180)	% error
										(mg/L)							
1	7.43	22.8	18400	0.00	440	380.0	3200	92.0	282.6	650.0	7.70	6200	51.0	0.5	11152	12500	0.432
2A[1]	7.53	25.0	820	1.95	15	4.8	180	6.6	266.7	139.0	NA[3]	64	22.0	NA[3]	597	NA[3]	-5.640
2B	8.02	20.1	748	4.50	85	19.0	52	5.5	403.2	18.0	0.17	40	22.0	0.3	440	470	0.488
3	7.04	22.7	36800	0.00	420	920.0	7300	260.0	522.6	1700.0	56.25	13000	28.0	0.4	23885	25400	1.218
4	7.08	22.0	37900	4.70	400	940.0	7600	280.0	284.8	1700.0	4.00	14000	26.0	0.6	25086	26600	0.001
5	8.14	21.6	2450	0.00	24	52.0	380	28.0	318.6	62.0	70.00	580	34.0	1.2	1318	1350	-0.474
6	7.43	21.8	46200	2.00	400	1200.0	9600	380.0	297.2	2200.0	0.26	17000	13.0	0.6	30940	33200	1.460
7B[2]	7.60	22.8	2440	2.65	320	17.0	120	3.3	217.2	60.0	0.16	600	56.0	0.2	1285	1740	2.158
7C[2]	7.41	22.8	3020	NA[3]	380	21.0	160	3.8	192.2	78.0	NA[3]	800	55.0	0.2	1593	2210	0.715
8	6.62	20.9	706	3.27	51	10.0	77	4.9	77.0	71.0	0.12	140	5.7	0.1	398	454	1.089
9	7.64	20.9	553	4.00	76	2.8	31	1.6	256.0	2.1	0.28	43	64.0	0.2	347	382	-0.469
10	7.92	20.9	547	2.05	75	10.0	25	2.1	255.2	41.0	0.55	29	36.0	0.3	344	358	-1.416
11	7.72	21.2	3790	1.80	500	28.0	200	4.9	168.6	95.0	0.50	1000	54.0	0.1	1965	2610	4.522

[1] All samples are from the December sampling event, except 2A, which is from the July sampling event, and is shown for seasonal comparison.
[2] Samples 7B and 7C from before and after 48-hour aquifer test, respectively.
[3] NA = Not Analyzed.

Table 2. Summary of the Hydrogeochemistry of Cumberland Island, Georgia.

Site	Well number	Aquifer	Water type	Suggested origin and dominant processes
1	1	Miocene Sand	Sodium-chloride	Seawater-freshwater mixing and sulfate reduction
	2	Surficial	Calcium-bicarbonate	Dissolution of calcite and aragonite sea shells
	3	Pliocene-Miocene	Sodium-chloride	Seawater-freshwater mixing and sulfate reduction
2	4	Pliocene-Miocene	Sodium-chloride	Seawater-freshwater mixing and sulfate reduction
	5	Surficial	Sodium-chloride	Low percentage seawater-freshwater mixing from occasional flooding of salt marsh and sulfate reduction
	6	Pliocene-Miocene	Sodium-chloride	Seawater-freshwater mixing and sulfate reduction
3	7	Pliocene-Miocene	Calcium-chloride	Low percentage seawater-freshwater mixing and reverse-ion exchange of calcium and sodium ions
	8	Surficial	Sodium-chloride	Low percentage seawater-freshwater mixing from sea spray
	9	Pliocene sand unit	Calcium-bicarbonate	Dissolution of carbonate sand aquifer matrix
	10	Lower confining bed	Calcium-bicarbonate	Dissolution of limestone aquifer matrix
	11	Pliocene-Miocene	Calcium-chloride	Low percentage seawater-freshwater mixing and reverse ion exchange of calcium and sodium ions

well sites. Well 2, which is located on the beach at site 1, was drilled within a poorly-sorted, fine-grained, siliceous sand. Traces of sea shells were observed in the drill cuttings. Sea shells were also observed in the sand at the surface. The groundwater composition at site 1 (well 2) resulted from the dissolution of calcium carbonate sea shells in the surficial aquifer. Well 5, a surficial-aquifer well located in a salt marsh on the southern end of the island, was drilled within a siliceous sand with approximately 5% heavy minerals and 5 to 15% calcitic and aragonitic shell fragments. The sodium-chloride water type at site 2 (well 5) is thought to result from the occasional flooding of the saltmarsh by seawater. The ocean water then percolates into the surficial aquifer and mixes with the freshwater already present to form a mixed water comprised of about 4% seawater. Well 8, the surficial-aquifer well at site 3, was drilled within a fine-grained, siliceous sand with traces of heavy minerals and mica. No sea shells or other sources of calcium carbonate were observed. The sodium-chloride water type at site 3 (well 8) probably results from sea spray being deposited in the vadose zone. The sodium, chloride, and other ions commonly found in seawater become concentrated in the vadose zone as the seawater evaporates, and eventually some of this high-salinity water recharges the surficial aquifer.

Well 2 was the only well that showed a drastic seasonal change between samplings in July and December (Table 1). A possible explanation for this involves the large amount of rainfall from a

hurricane that passed near Cumberland Island prior to the December sampling. The large influx of rainwater caused the dissolution of calcitic and aragonitic sea shells found in the sand near the beach. The rainwater dissolved the sea shells, which caused high calcium- and bicarbonate-ion concentrations in the surficial aquifer. The sodium, potassium, sulfate, and chloride concentrations, that dominated the groundwater composition during July, and which are normally contributed to the surficial aquifer by sea spray, were diluted by the massive influx of freshwater in December. Well 5 showed a similar trend toward increased calcium and bicarbonate concentrations, with decreased sodium and chloride concentrations between July and December; however, the relative changes in concentration were much lower than in well 2. It is important to note that the other surficial well, 8, showed very little or no seasonal variation in the concentrations of its major constituents. The storm that apparently flooded the surficial aquifer at site 1 with freshwater rain, had only a minor effect on site 2, and little or no effect on site 3. This is probably indicative of differences in rainfall and recharge over the island. It is also possible that normal rainfall differences of summer and winter could cause the previously discussed differences in surficial aquifer groundwater composition.

One notable difference between well 5 and the other surficial-aquifer wells (wells 2 & 8) is that well 5 is anaerobic. The sulfide content was significantly greater in well

5 (S^{2-} = 70 mg/L) than in either wells 2 or 8 (S^{2-} = 0.17 and 0.12
mg/L, respectively; Table 1). The anoxic conditions and the high
sulfide content in well 5 indicate sulfate reduction, a process
that is not possible in the aerobic conditions of wells 2 and 8.
It is not unusual for a saltmarsh to be anoxic, but it serves as
a good example of the heterogeneity of the surficial aquifer, and
the different geochemical processes that can occur in localized
areas on Cumberland Island.

Freshwater-Saltwater Interface in the Surficial Aquifer

The freshwater-saltwater interface was not observed in the
surficial aquifer, indicating that it must occur seaward of the
well sites. The surficial aquifer groundwater at site 2 (well 5)
contained about 3% seawater. The seawater percentage was
calculated by dividing the chloride-ion concentration of the
sample by the chloride-ion concentration of average seawater
(average seawater composition from Nordstrom et al., 1979; Table
3). Well 5 is located within the surficial aquifer at site 2,
which is in a high saltmarsh on the southern end of Cumberland
Island. Although this well contained a low percentage of
seawater in the groundwater samples, it was not interpreted to be
part of a mixing zone associated with a freshwater-saltwater
interface because water-level measurements on different dates
showed no tidal fluctuations. The saltwater content can also
easily be explained by the occasional flooding of the saltmarsh
by seawater. This seawater then

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Table 3. Composition of seawater (from Nordstrom et al., 1979).

Element	Concentration (ppm)
Ca	412
Mg	1291
Na	10768
Cl	19353
HCO_3	141
SO_4	2712
SiO_2	4

mixes with the fresh groundwater within the surficial aquifer.

Pliocene-Miocene Aquifer

The Pliocene-Miocene aquifer immediately underlies the
undifferentiated Pleistocene clay confining unit of the surficial
aquifer. The Pliocene-Miocene aquifer is composed of sands of
the Pliocene Duplin Formation equivalent and a layer of
fossiliferous dolomite of the Miocene Charlton Formation beneath
the sands (McLemore et al., 1981). The Pliocene sand unit of
this aquifer was only encountered at site 3 (well 9; Figure 3),
and was not encountered at either site 1 or 2, indicating that it
is not present in the southern portion of the island. However,
this unit is reportedly extensive north of site 3 until it
pinches out at the northern and western extremes of the island
(McLemore et al., 1981). This Pliocene sand unit is composed of
a medium-grained, calcareous sand. Sea shell fragments were
recovered from this unit; however, the exact percentage
composition could not be determined from the drill cuttings. A
clay confining bed, that was not reported by McLemore et al.
(1981), was encountered beneath the Pliocene sand aquifer at site
3. An aquifer test, using well 7 at site 3 as the pumping well,
indicated that leakage occurred from the Pliocene sand unit into
the underlying limestone-dolomite unit during the test;
therefore, the intermediate clay unit is not completely
confining.

Beneath this clay bed is the Miocene Charlton Formation. The

upper few feet of this dolomite unit often contained a highly fossiliferous zone of calcitic and aragonitic shells, as well as molds and casts. Zones of vugs, fractures, and cavities were also encountered within this unit. Beneath the zones of fossiliferous and vuggy dolomite, a layer of dense, often argillaceous, sandy dolomite was encountered. This unit, which varied from 15 to 40 feet (4.6 to 12.2 m) in thickness, is interpreted to be the lower confining bed of the Pliocene-Miocene aquifer (Figure 3).

At site 1, well 3 was drilled within the Pliocene-Miocene aquifer from 79 to 94 feet (24.1 to 28.7 m) (below land surface; Figure 5). Well 4 at site 2 also screens a 79 to 94 - foot (24.1 to 28.7 m) deep interval that drill cuttings indicate is an argillaceous dolomite. At both sites, the groundwater from this interval is 67% (well 3) and 72% (well 4) seawater. These percentages, which are based on chloride content, indicate the intrusion of seawater into the 79 to 94 -foot, confined aquifer and the mixing of freshwater with seawater to dilute it to these percentages. The 67 to 72% seawater also indicated that a zone of dispersion was present within the aquifer. The composition of the mixed water at any given point in the mixing zone depended on the location of that point relative to the seawater and freshwater fronts. For example, wells 3 and 4 were closer to the seawater front than the freshwater front in the mixing zone as indicated by the high percentages of seawater present in those wells (Figures 5 & 6).

Figure 5. - Cross-section of Well Site 1 and Navigation Channel
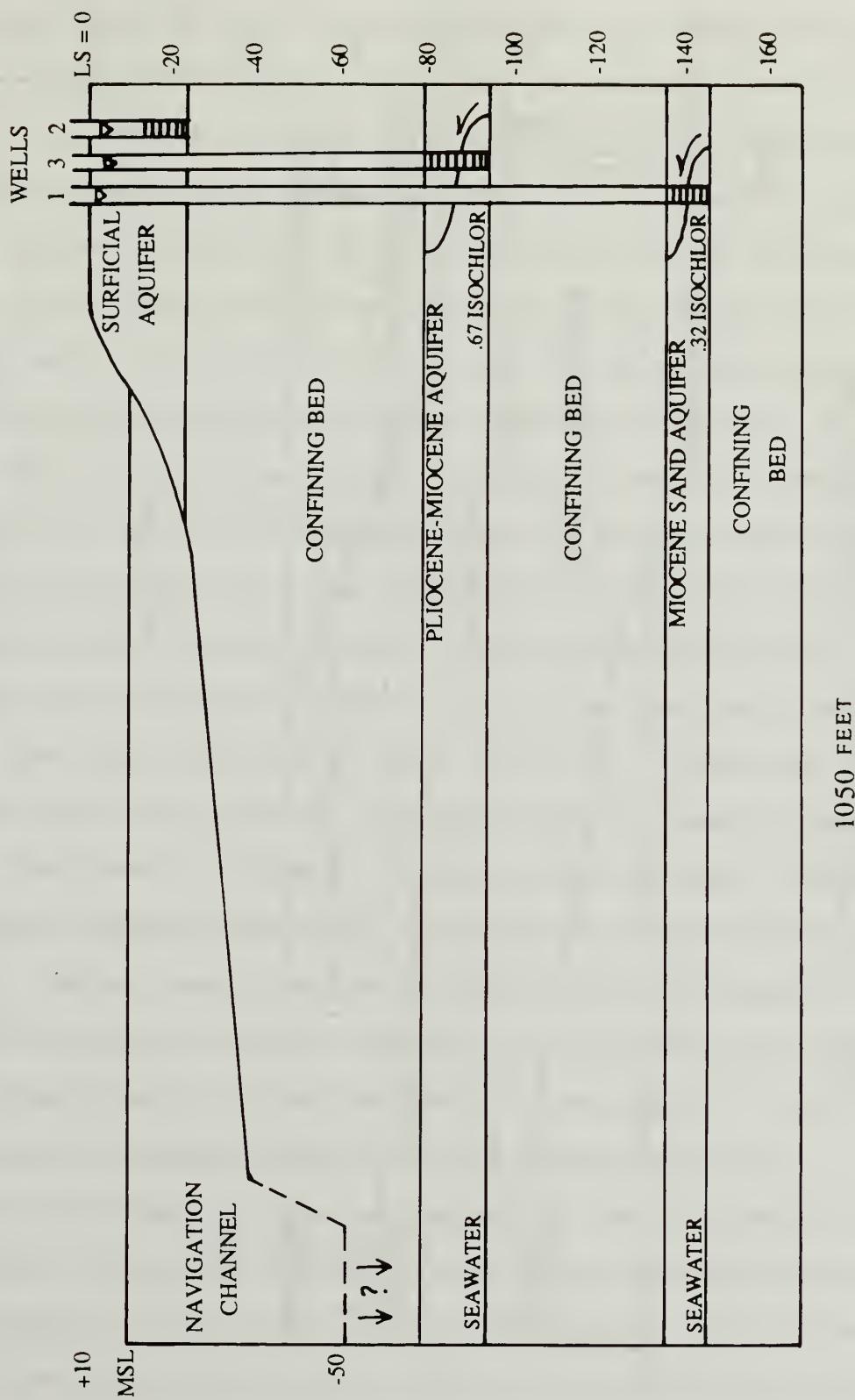
Figure 6. - Cross-section of Well Site 2 and Navigation Channel

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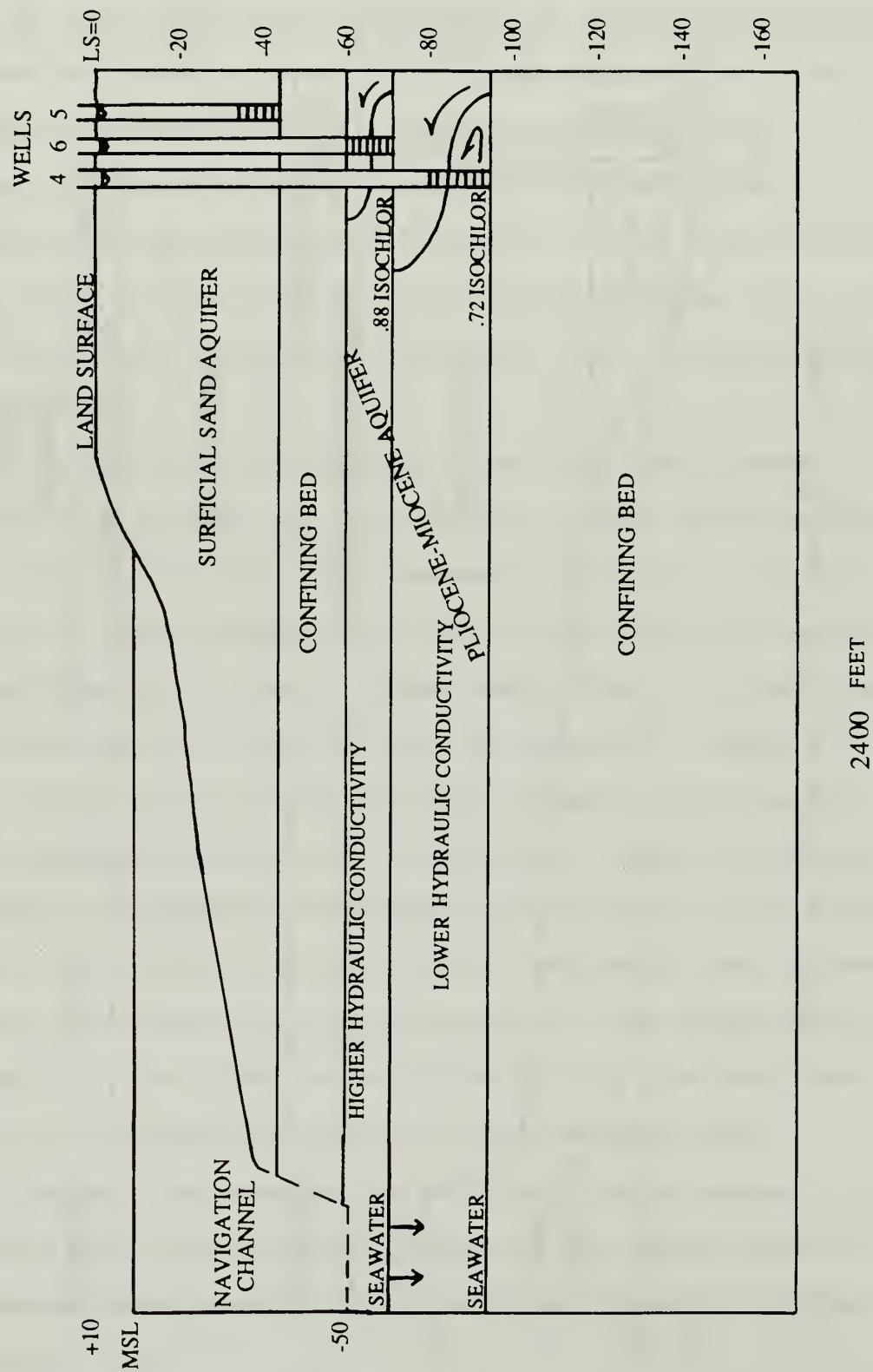
Well 6 is located at site 2 and screens an interval from 61 to 71 feet (18.6 to 21.6 m). The ground-water from this well is 88% seawater. This indicates that the well is located close to the seawater front within the zone of dispersion in this aquifer. Well 6 had a higher seawater content (88%) than well 4 (72%), which is located in the same cluster and was drilled in the 79 to 94 - foot (24.1 to 28.7 m) zone (Figure 6). The higher seawater content in well 6 is attributable in part to the higher hydraulic conductivity and, therefore, greater seawater intrusion, in the region of well 6, as opposed to the region of well 4. Sampling of both wells at a rate of approximately 15 gallons (56.8 L) per minute revealed that well 4 had difficulty maintaining that output, while well 6 had no trouble. A comparison of the hydraulic heads in wells 6 and 4 revealed that they are very similar. The hydraulic head in well 6 (61 to 71 feet) was 3.25 feet (1 m) below land surface, and the hydraulic head in well 4 (79 to 94 feet) was 3.3 feet (1 m) below land surface. The similar heads suggest that these units may be hydraulically connected. Wells 4 and 6 may be located within different permeability zones of the same aquifer, or alternatively, well 4 may be located within a lower permeability aquiclude or aquitard. With its higher seawater percentage and greater apparent transmissivity (based on pumping the wells), well 6 appeared to be in a higher hydraulic conductivity dolomite zone than well 4. Cuttings sampled every 10 feet (3.0 m) during the drilling of both wells showed no lithological differences between the two,

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but a resistivity geophysical log showed a much greater resistivity in the 61 to 71 - foot (18.6 to 21.6 m) zone (log on file with the USGS-WRD, Atlanta, GA). Since resistivity logs can be the inverse of normal resistivity in highly saline environments, this peak resistivity value in the 61 to 71 - foot (18.6 to 21.6 m) zone corresponds to the high saltwater content of the zone. This peak was not present in the 79 to 94 - foot (24.1 to 28.7 m) zone.

Wells 7 and 11 at site 3 (Figure 1) were drilled within the Pliocene-Miocene aquifer. The groundwater samples from both of these wells contained a seawater component. A 48-hour aquifer test of this zone was conducted during the December, 1989, sampling event using well 7 as the pumping well. Groundwater samples were taken before and after the test, and were labelled 7B and 7C, respectively. Well 11 (90 to 95 feet [27.4 to 28.0 m]) already existed at the beginning of this project, and was sampled after the aquifer test. Sample 7B, which was taken before the aquifer test, contained about 3% seawater. Sample 7C, which was taken immediately after the 48-hour aquifer test, contained about 4% seawater. Sample 11 contained about 5% seawater. This information clearly indicates that the source of the seawater contamination is northwest of well 7 in the direction of well 11, and that the 48-hour aquifer test increased the seawater percentage present in well 7. These wells were drilled within the zone of dispersion for the Pliocene-Miocene aquifer, and the low seawater percentages indicate that they must

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be near the freshwater front in the zone of dispersion. This indicates that significant landward intrusion of seawater has occurred. This intrusion may be the result of pumping of this aquifer for water supply purposes, or the exposure of the aquifer to seawater offshore of the island. These factors are not mutually exclusive, and both may have contributed to the seawater intrusion. The pumping of the Pliocene-Miocene aquifer for domestic supply, as well as the aquifer test, may have changed the hydraulic gradient from the southeasterly (seaward) direction to the opposite direction, which would contribute to seawater intrusion.

Geochemistry: Previous Work

The major ion chemistry of the Pliocene-Miocene aquifer of Cumberland Island was previously analyzed by McLemore et al. (1981). The values listed in Appendix II represent a mean for all samples collected, but neither the number of samples, the average depth, nor the location of wells sampled is provided in the report. These factors made comparison of the data with the results of this study difficult.

Geochemistry of the Upper Sand Unit and the Lower Confining Bed of the Pliocene-Miocene Aquifer

The Pliocene sand unit of the Pliocene-Miocene aquifer was monitored by well 9 (61 to 71 feet [18.6 to 21.6 m]) at site 3 (Figure 3). The groundwater within this sand was a dilute,

fresh, calcium-bicarbonate type groundwater (Tables 1 & 2; Figure 7). The groundwater composition of well 9 was probably representative of the freshwater composition of the Pliocene-Miocene aquifer before mixing with seawater in the zone of dispersion. Simple mixing of freshwater with seawater should produce a "straight-line dilution" of seawater. The figures in this report show a "straight line dilution" to an end member with zero ion concentrations, rather than well 9. It is important to note that the ionic concentrations of well 9 (with the exception of bicarbonate, which is mainly a function of carbon dioxide partial pressure) were on the seawater dilution line near zero. This is not meant to imply that well 9 was diluted seawater, but to illustrate that well 9 was a probable freshwater end member, and that slight deviations from the zero-end member used in the figures did not alter the conclusions of this report. The groundwater from well 10 (123 to 133 feet [37.5 to 40.5 m]), that was drilled within a sandy clay confining bed beneath the Pliocene-Miocene aquifer, was also a very dilute, calcium-bicarbonate type groundwater (Tables 1 & 2). The geochemical composition of the water from these two units was very similar (Figure 8). The most important difference between the two wells was the higher sulfate content in well 10 (SO_4^{2-} = 41 mg/L) compared to well 9 (SO_4^{2-} = 2.1 mg/L) (Table 1). All of the other constituents were very similar (Table 1). The geochemical similarity of two stratigraphically distinct units tended to confirm that the groundwater of the Pliocene-Miocene

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FIGURE 7

Trilinear Diagram of Ground-Water Composition
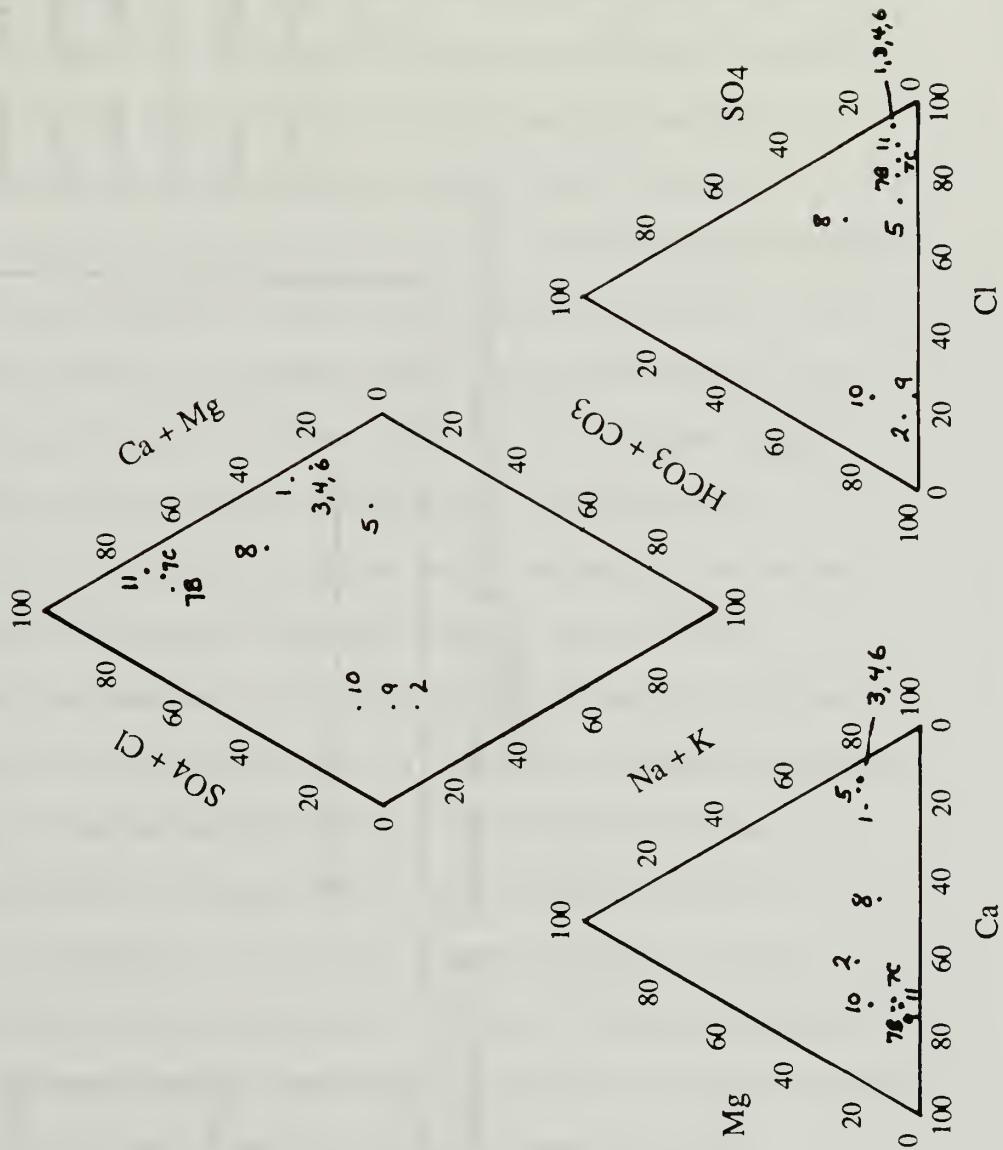
FIGURE 8

Comparison of Samples from Wells 9 (63-73') and 10 (123-133')
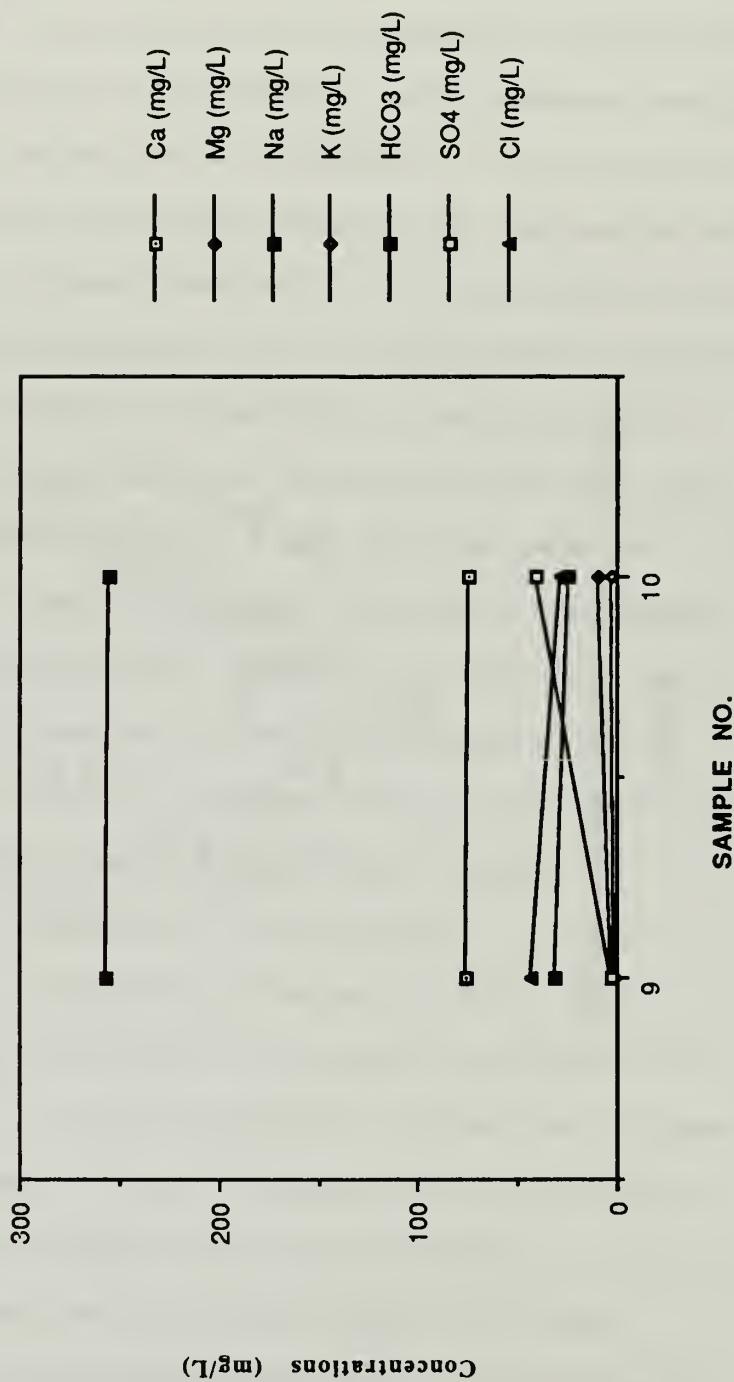
aquifer, and probably the Miocene sand aquifers, was a dilute, fresh calcium-bicarbonate groundwater before mixing with seawater in the zone of dispersion.

Several reasons for the similar groundwater compositions are possible. The first possibility is that faulty well construction allowed leakage into well 10 from the Pliocene sand unit (well 9). However, faulty well construction would not allow the contamination of well 10 by the Pliocene sand unit without a contribution from the dolomite aquifer (well 7) that lies between that unit and the zone tapped by well 10 (Figure 3). No geochemical evidence exists to support the theory that well 10 was being contaminated by any of the other wells in the cluster. Therefore, this possibility is not feasible. The second possibility is that both (9 & 10) units were actually the same carbonate sand aquifer that has become locally divided and confined by the complex geology of the barrier island. Another possibility is that all four wells (7, 9, 10, & 11) were drilled within one large heterogeneous aquifer that contained zones of higher and lower hydraulic conductivity that vary with the lithology. The high permeability units are at least locally confined and separated from each other. The groundwater present in wells 7 (82 to 89 feet [25.0 to 27.1 m]) and 11 (90 to 95 feet [27.4 to 29.0 m]) has become geochemically altered by the seawater intrusion of the limestone-dolomite unit, while the compositions of the carbonate sand of well 9 or the sandy-clay of well 10 remained unaltered.

An aquifer test of well 7 revealed that local confining units exist between all three depths. Well 10 showed no response to the pumping of well 7, and maintained the same hydraulic head. The hydraulic head in well 9 decreased in response to the pumping of well 7, and some leakance occurred into the fossiliferous dolomite. This indicates that wells 9 and 10 were not hydraulically connected.

Geochemistry of the Zone of Dispersion in the Pliocene-Miocene Aquifer: The Freshwater Region of the Mixing Zone

As previously mentioned, the fossiliferous dolomite zone of the Pliocene-Miocene aquifer is stratigraphically located between the overlying sand unit monitored by well 9 and the underlying confining bed monitored by well 10. This zone was monitored by wells 7 and 11. Well 11 (90 to 95 feet [27.4 to 29.0 m]) was constructed prior to this project. Conversations with National Park Service employees on Cumberland Island indicated that well 11 was a freshwater well used for drinking and domestic purposes. After several years of use, the well water became salty, and its use was discontinued.

The groundwater composition of this zone before and after the aquifer test indicated a calcium-chloride water type (Table 2) that resulted from a combination of the mixing of carbonate groundwater with seawater, and subsequent-reverse ion exchange. A comparison of samples 7B, 7C, and 11 clearly showed that the aquifer test caused an increase in the concentrations of all

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constituents in well 7 except bicarbonate, and that these increases were proportional to the concentrations present in well 11 (Figure 9). Chloride concentrations indicate that these samples contained 3 to 5% seawater (Table 1). The decrease in bicarbonate concentration (Figure 9) would be expected in freshwater mixing with a small percentage of seawater (Appelo and Willemsen, 1987). The conclusion reached from this evidence is that the freshwater present in the limestone-dolomite unit is mixing with a small percentage of seawater. The mixing with seawater caused an increase in all major constituents except bicarbonate, which decreased. The general direction of the contamination is assumed to be northwest of well 7, in the direction of well 11.

When the saltwater mixes with the freshwater, sodium and chloride should become the dominant ions in solution. However, the water types in samples from wells 7 and 11 were calcium-chloride, rather than sodium-chloride (Table 2). Reverse-ion exchange appears to have altered the freshwater-saltwater mixture in the region of wells 7 and 11 by replacement of the sodium and potassium ions from the mixed water with calcium ions from the aquifer matrix. The evidence for this process is the lower-than-simple-mixing concentrations of sodium and potassium (Figures 10 & 11), and the higher than simple mixing concentration of calcium in solution (Figure 12). No process other than reverse-ion exchange could account for these trends.

FIGURE 9
Comparison of Samples from Wells 7 & 11 at Site 3
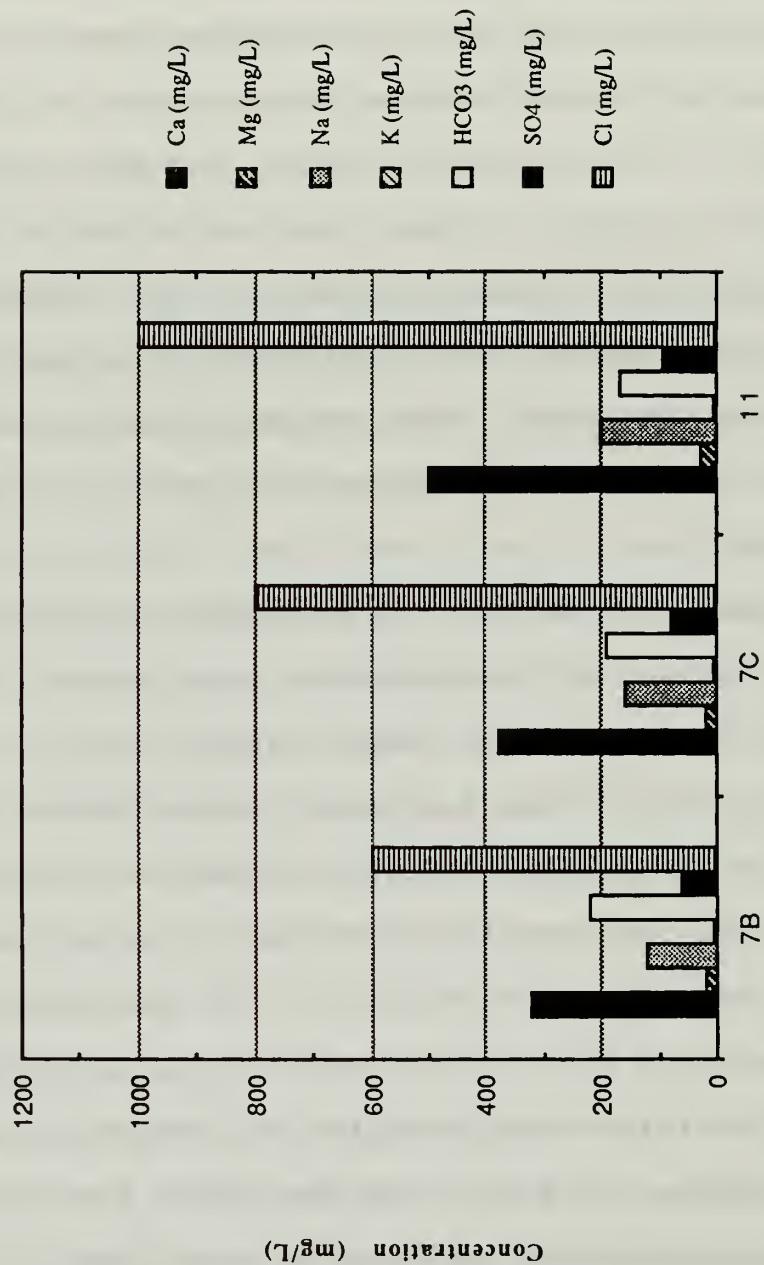
Sample 7B taken before aquifer test, sample 7C taken after aquifer test, sample 11 taken after aquifer test

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FIGURE 10
Graph of Sodium vs. Chloride ion concentrations
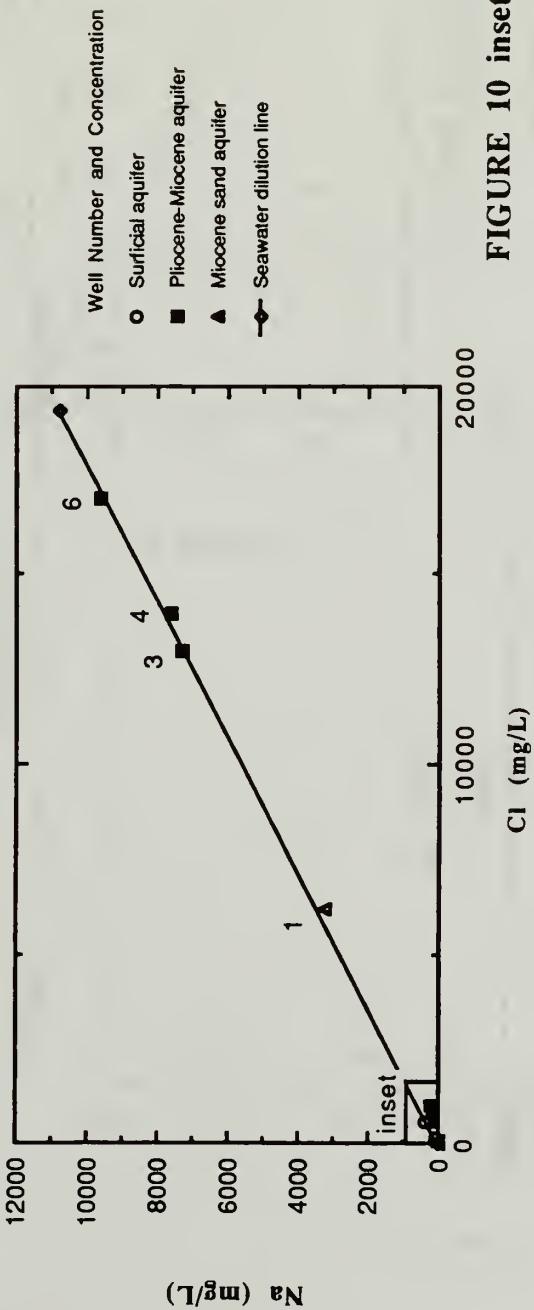
FIGURE 10 inset
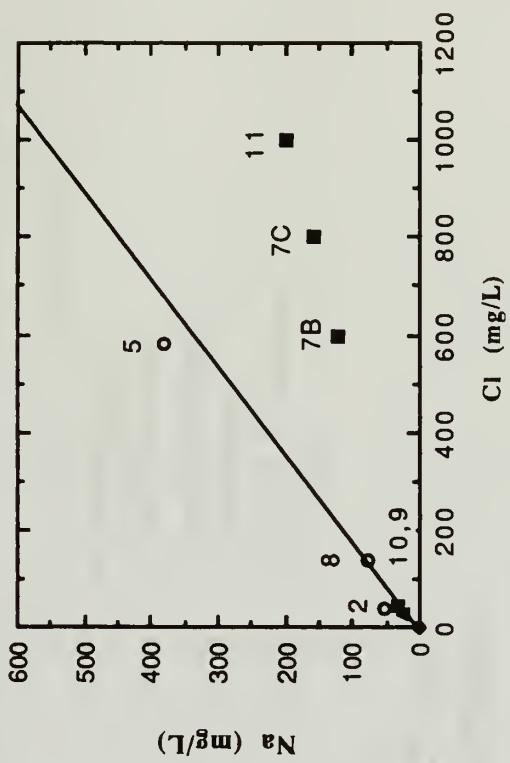
FIGURE 11
Graph of Potassium vs. Chloride ion concentrations

FIGURE 11 inset

Well Number and Concentration
○ Surficial aquifer
■ Pliocene-Miocene aquifer
▲ Miocene sand aquifer
◆ Seawater dilution line
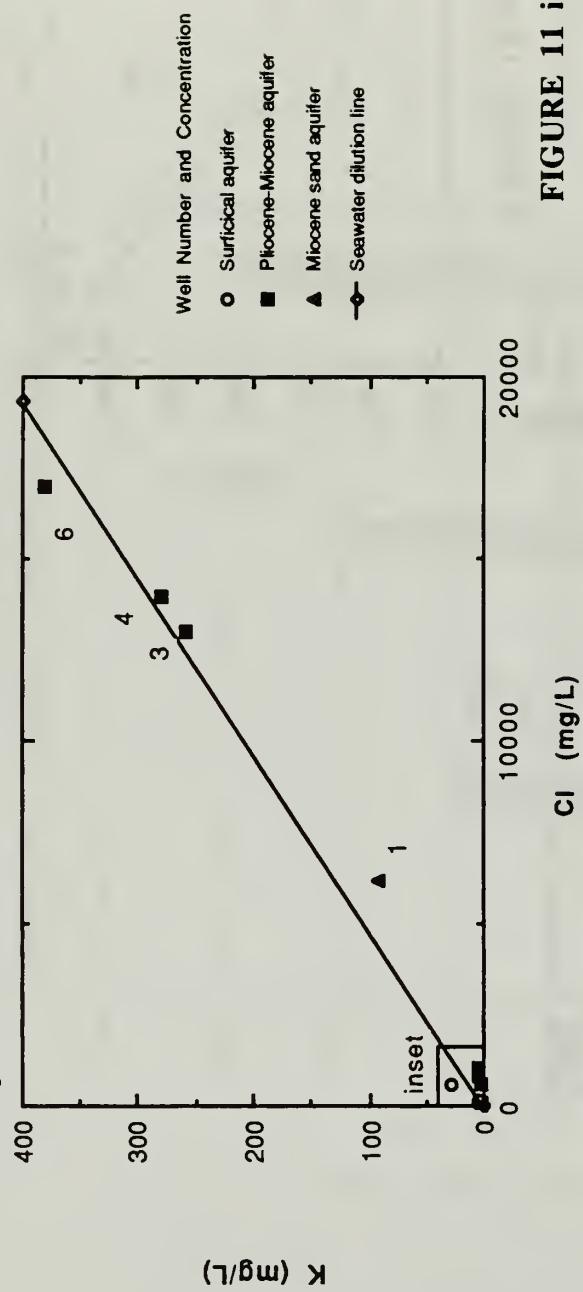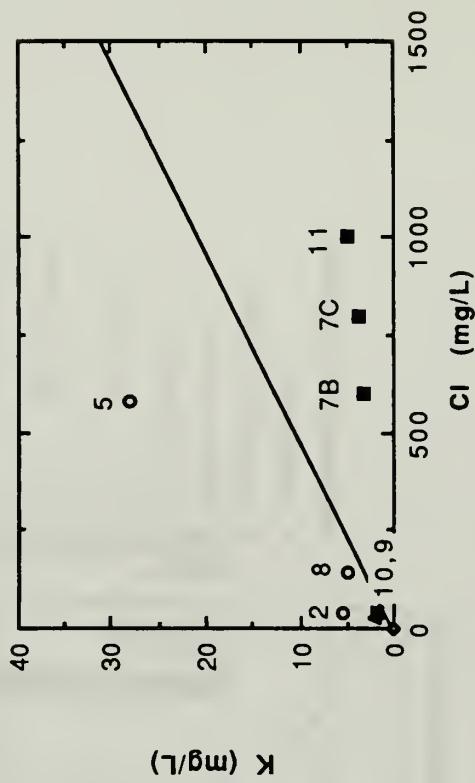
FIGURE 12
Graph of Calcium vs. Chloride ion concentrations
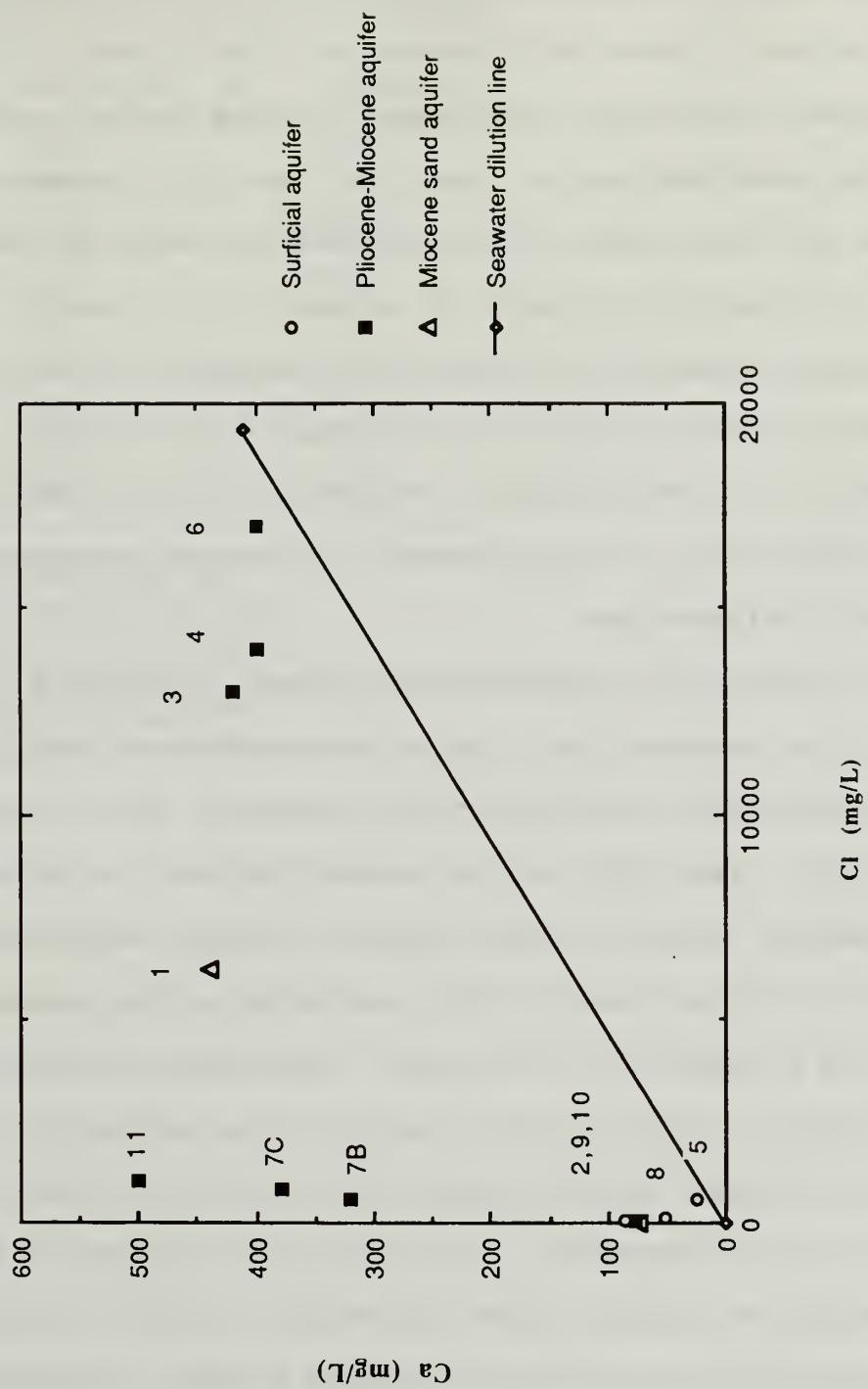
Interestingly, no evidence of reverse ion exchange was observed in the mixing zone wells (1, 3, 4, & 6) along the coast of the island. These wells contained significantly higher percentages of seawater, and significantly higher ionic concentrations than wells 7 and 11. The high percentages of seawater and high ionic concentrations may explain the apparent lack of reverse-ion exchange in wells 1, 3, 4, and 6, as well as the apparent presence of reverse-ion exchange in wells 7 and 11. This implies that reverse ion exchange only occurred in the freshwater (3 to 5% seawater) region of the zone of dispersion, and did not occur in the seawater (66 to 88% seawater) region of the zone of dispersion.

The calcium-ion concentrations present in samples 7B, 7C, and 11 were much greater than simple two-end-member mixing of a calcite-saturated groundwater with seawater would indicate (Figure 12). The high calcium concentrations in wells 7 and 11 were probably caused by two factors: calcium carbonate dissolution in the mixing zone, and reverse-ion exchange of sodium and potassium for calcium. These high calcium concentrations indicated that calcitic and aragonitic shells in the fossiliferous dolomite must have been dissolved in this portion (3 to 5% seawater) of the zone of dispersion because no other source of calcium ions was present within the aquifer. This dissolution of calcium carbonate probably occurred in the mixing zone even though the groundwater was supersaturated with respect to calcite and aragonite (Table 4). Although this

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Table 4. Comparison of the
saturation indicies of Cumberland
Island groundwater samples (December).

Sample number	S.I. calcite	S.I. dolomite
1	.527	1.344
2	.965	1.572
3	.250	1.213
4	-.004	.727
5	.357	1.367
6	.318	1.483
7B	.778	.612
7C	.584	.242
8	-.452	-3.050
9	.412	-.310
10	.656	.741
11	.886	.883

The sample number listed above is the same
as the respective well number except for
samples 7B and 7C. Sample 7B was taken from
well 7 before the aquifer test discussed in the
text, and sample 7C was taken after the aquifer
test. All samples are from the December
sampling period. Saturation Index = Log_{10} Ion
Activity Product / Equibrium Constant as
calculated by WATEQF (Plummer et al., 1976).

situation appeared to be contradictory, the kinetics of this situation were more important than the thermodynamics in determining the actual reactions occurring in this portion (3 to 5% seawater of the mixing zone. Previous works by Plummer (1975) and Wigley and Plummer (1976) have shown that the pCO_2, pH, ionic strength, and temperature of freshwater-seawater mixtures have a nonlinear and cumulative effect on calcite solubility and undersaturation. The combination of high pCO_2 (log pCO_2 of wells 7 & 11 = -2.21 to -2.61 atm.), relatively low pH (pH = 7.42 to 7.72), high ionic strength (= 0.0303 to 0.0472), and low temperature (21.2 to 22.8°C) in the freshwater region of the Pliocene-Miocene aquifer mixing zone resulted in initial undersaturation of the mixture and dissolution of calcium carbonate, which dramatically increased the calcium ion concentrations in the groundwater. This undersaturation apparently occurred as the freshwater and seawater initially mixed. The combined effects of the high pCO_2, the relatively low pH, the low temperature, and the high ionic strength of the mixture drove the dissolution of $CaCO_3$ past equilibrium to the point that the groundwater was supersaturated with respect to calcite. This dissolution and subsequent supersaturation produced the higher-than-simple-mixing concentrations of calcium and bicarbonate ions in solution (Figures 12 and 13), as well as saturation indicies greater than zero (Table 4). Although the groundwater was supersaturated with respect to calcite, calcite probably did not precipitate in the mixing zone because the aquifer permeability and, therefore, the ground-water

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FIGURE 13
Graph of Bicarbonate vs. Chloride ion concentrations

Well Number and Concentration

- ○ Surficial aquifer
- ■ Pliocene-Miocene aquifer
- ▲ Miocene sand aquifer
- ◆ Seawater
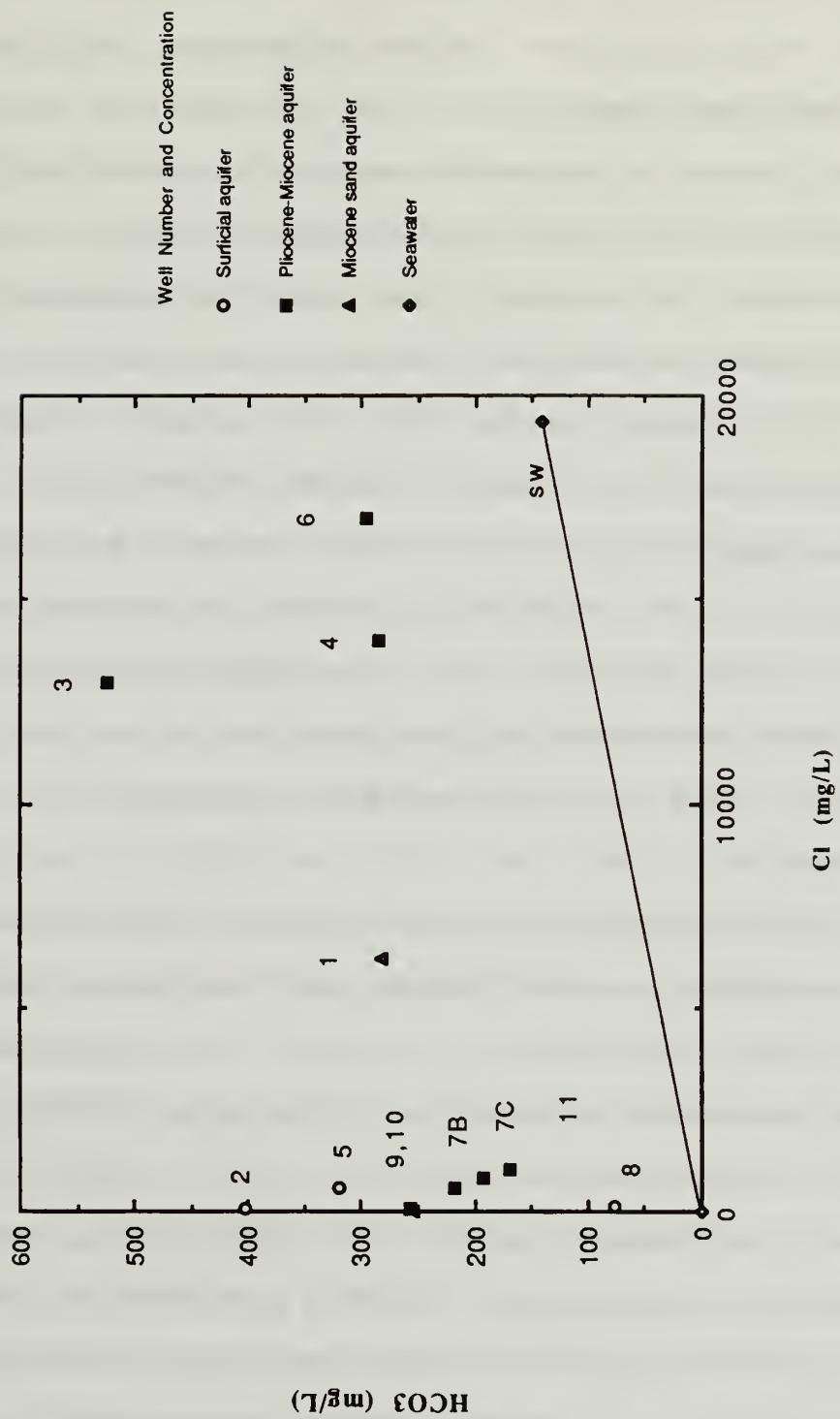
flow velocity, was apparently high enough that the mixture did not have time to equilibrate and precipitate calcite before it left the mixing zone and was discharged into the ocean. The high groundwater flow velocity (as inferred from the 48-hour aquifer test) in the Pliocene-Miocene mixing zone appeared to be the result of relatively high hydraulic gradient, density convection, and tidal fluctuation. This theory is supported by previous simulation of calcite dissolution in a mixing zone in which calcite dissolution was found to increase linearly with increased groundwater flow velocity (Sanford and Konikow, 1989b). A high groundwater flow velocity would not only partially explain the CaCO$_3$ dissolution and high calcium-ion concentration present in the mixing zone, but would also explain the apparent lack of calcite and aragonite precipitation in the mixing zone even though the mixed water was supersaturated with respect to these minerals.

It is also apparent from Figure 12 that the calcium-ion concentration increased rapidly with increasing seawater percentage (chloride concentration) in the 3 to 5% seawater mixtures. As the percentage of seawater in the zone of dispersion increased past 5%, as shown by wells 3, 4, and 6, the calcium-ion concentrations gradually decreased. This compares favorably with computer simulations by Sanford and Konikow (1989a & b) in which calcite dissolution in mixing zones was found to increase rapidly in mixtures up to approximately 5% seawater, increase slowly in mixtures of approximately 5 to 20% seawater, and decrease slowly

at percentages greater than 20% seawater.

The Saltwater Region of the Mixing Zone

The geochemistry of the wells (3, 4, & 6) drilled within the seawater region (66 to 88%) of the zone of dispersion within the Pliocene-Miocene aquifer can be explained as the mixing of two-end members: one freshwater and the other seawater. The ground-water samples from each of these wells were calcium-bicarbonate water type. All of the samples from these wells exhibited substantially greater concentrations of calcium and bicarbonate ions than those predicted by simple mixing of two end-members (Figures 12 & 13). The sulfate concentrations were lower than simple mixing would indicate (Figure 14). In contrast, the magnesium, sodium, and potassium concentrations were consistent with the mixing of two-end members (Figures 10, 11, & 15). Therefore, some process or processes other than simple mixing must be responsible for the increased concentrations of calcium and bicarbonate ions, as well as the reduced sulfate-ion concentration.

A process that probably contributed to the high bicarbonate- and low sulfate-ion concentrations found in these mixing zone wells (3, 4, & 6) was sulfate reduction. Well 3, anaerobic conditions existed thus permitting sulfate reduction, as evidenced by sulfate concentrations that were slightly lower than predicted by simple mixing of end members (Figure 14). Sulfate concentrations that were slightly lower than predicted were also

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FIGURE 14
Graph of Sulfate vs. Chloride concentrations
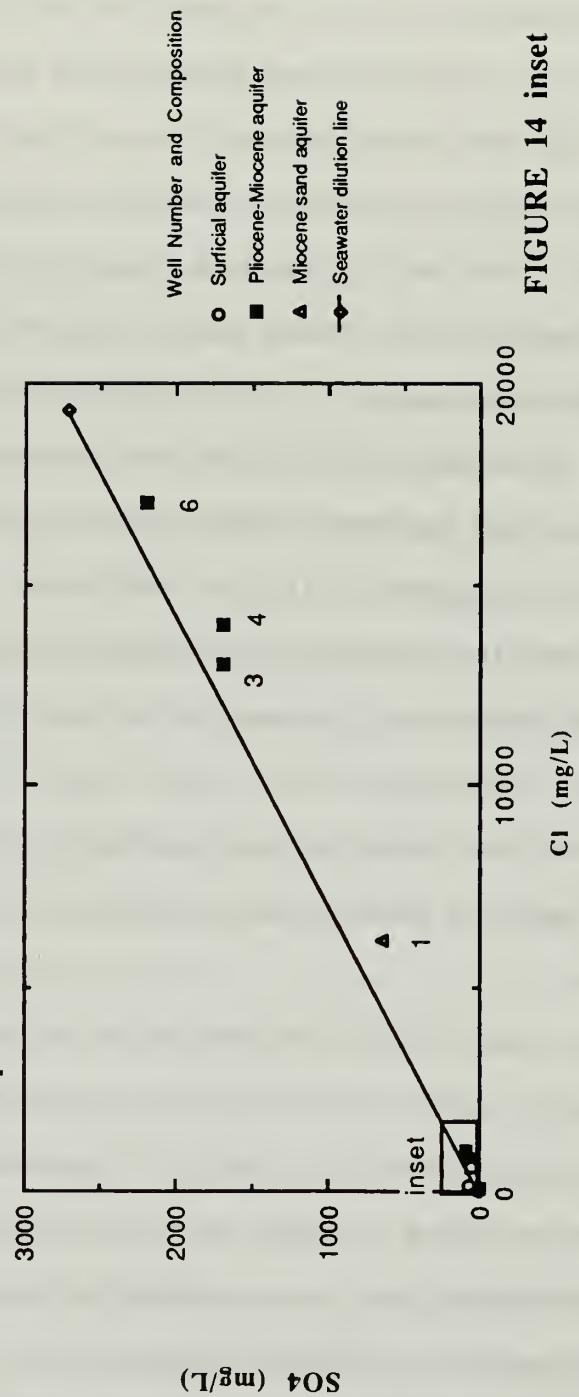
FIGURE 14 inset
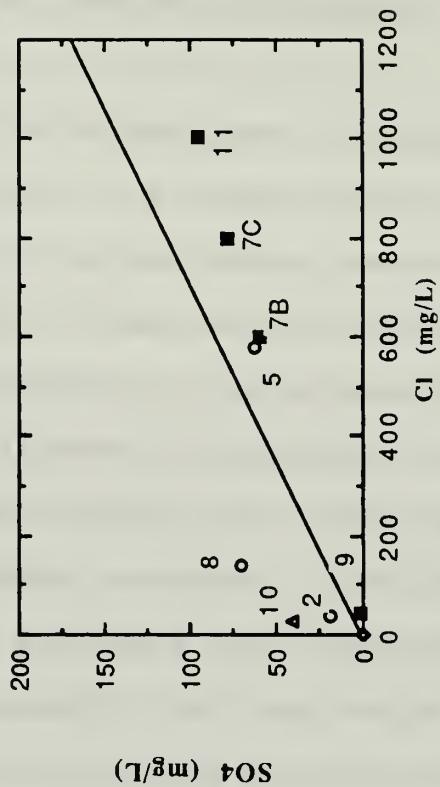
FIGURE 15

Graph of Magnesium vs. Chloride ion concentrations

FIGURE 15 inset

Well Number and Concentration
- ○ Surficial aquifer
- ■ Pliocene-Miocene aquifer
- ▲ Miocene sand aquifer
- ◇ Seawater dilution line
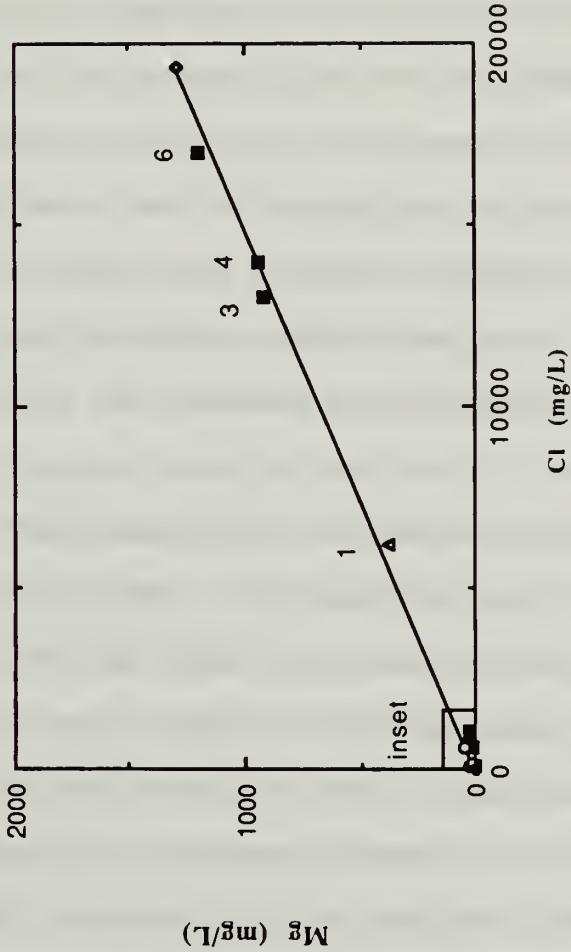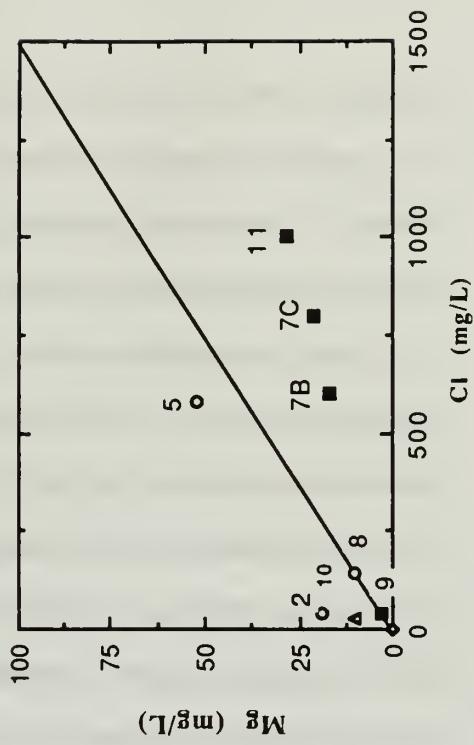
encountered in wells 4 and 6 (Figure 14), which are aerobic (DO = 4.7 and 2.0 mg/L, respectively). Since sulfate reduction cannot occur in aerobic zones, the sulfate was probably being reduced before the groundwater flowed into the region around wells 4 and 6. This reduction was occurring in anaerobic zones along the flow path which were created by microbial respiration which consumed oxygen. The only other explanation for the low sulfate concentrations would be the precipitation of sulfate-bearing minerals, such as gypsum or anhydrite; however, no sulfate-bearing minerals were observed in the drill cores and cuttings, and no mention of such minerals was made by previous workers. Therefore, sulfate reduction was probably the cause of the lower-than-predicted sulfate concentrations. Since sulfate reduction produces bicarbonate, it was probably a contributing process to the high bicarbonate concentrations observed in the mixing zone wells (3, 4, & 6).

The high concentrations of calcium and bicarbonate ions in these wells (3, 4, & 6) were probably the result of $CaCO_3$ dissolution. Calcium carbonate is present within the aquifer matrix of all three of these wells, and its initial dissolution would provide calcium and bicarbonate ions to the mixed waters with very little effect on the concentrations of the other ions in solution. The high pCO_2 (log pCO_2 = -1.54 to -2.21 atm. [Table 1]), relatively low pH (pH = 7.04 to 7.43), low temperature (21.8 to 22.7°C), and high ionic strength (0.466 to 0.605) present within these mixing-zone waters resulted in the initial undersat-

uration and dissolution of $CaCO_3$. This initial undersaturation apparently occurred as the freshwater and seawater first mix. The high pCO_2, the relatively low pH, the low temperature, and the high ionic strength of the mixture drove the dissolution reaction of $CaCO_3$ past equilibrium to the point that the ground-water was supersaturated with respect to calcite. In the higher hydraulic conductivity regions (wells 3 & 6), the apparently high groundwater flow velocity probably contributed to the other factors that caused the dissolution of $CaCO_3$ past equilibrium to supersaturation. This dissolution produced the higher-than-simple-mixing concentrations of calcium and bicarbonate ions in solution (Figures 12 & 13). Although the groundwater was super-saturated with respect to calcite, precipitation probably did not occur because any precipitation of calcite would decrease the concentrations of calcium and bicarbonate ions in the groundwa-ter. Such decreases were not evident in wells 3 or 6, as shown by Figures 12 and 13. The flow velocity in these wells was also apparently high enough to prevent the equilibration of the supersaturated mixed water with calcite and, therefore, calcite precipitation. This situation was similar to the previously discussed freshwater region of the mixing zone (wells 7 & 11). The groundwater flow velocity, resulting from the hydraulic gradient, tidal fluctuation, and density convection, was high enough in wells 3 and 6 to circulate the water through the zone of dispersion and discharge it into the ocean before calcite precipitation could occur.

In the lower hydraulic conductivity region of well 4, $CaCO_3$ dissolution probably occurred as the result of high $pCO2$, relatively low pH, low temperature, and high ionic strength. This dissolution increased the concentrations of calcium and bicarbonate ions in the mixed water; however, unlike wells 3 and 6, dissolution occurred only until equilibrium was reached (S.I.calcite = -0.004) (Table 4). Therefore, the inferred relatively low groundwater flow velocity in the region of well 4 allowed the mixing-zone water to equilibrate with calcite, while the higher flow velocities in the regions of wells 3 and 6 caused the mixing-zone water to dissolve enough $CaCO_3$ to become supersaturated with respect to calcite and aragonite. Alternatively, dissolution to supersaturation may have occurred, but the groundwater flow velocity in the low-hydraulic conductivity region was insufficient to discharge the water through the mixing zone and into the ocean before it could equilibrate with respect to calcite. Either situation indicated that groundwater flow velocity was an important factor in the dissolution and precipitation in mixing-zone waters. Either situation would also explain the supersaturation of the groundwater with respect to calcite in the region of wells 3 and 6, and the equilibrium with respect to calcite in the region of well 4.

The mixing zone of the Pliocene-Miocene aquifer in the low-hydraulic conductivity region of well 4 is the only region in which the groundwater is undersaturated with respect to aragonite (S.I. = -1.50), in equilibrium with respect to calcite (S.I. = -0.004),

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and supersaturated with respect to dolomite (S.I. = 0.727). As previously discussed, $CaCO_3$ dissolution and equilibrium had occurred in the region around well 4. A mixing-zone water, such as this, that is undersaturated with respect to $CaCO_3$ and super- saturated with respect to dolomite has the thermodynamic poten- tial for dolomitization by dissolution of $CaCO_3$ and precipitation of dolomite (Hanshaw et al., 1971). The "Dorag" dolomitization model (Badiozamani, 1973) predicted dolomitization by replacement in mixed-water compositions of 5 to 30% seawater. Stoessel et al. (1989) showed that certain mixed-water compositions of 5 to 90% have the potential for replacement of limestone by dolomite. The 72% seawater composition of well 4 was much higher than the percentages predicted by Badiozamani (1973), but was within the range reported by Stoessel et al. (1989). A Mg/Ca ratio greater than 1 or 3 is another important factor in dolomitization (Hans- haw et al., 1971; Hanshaw and Back, 1979). The Mg/Ca ratio was 3.87 (from data in Table 1) in sample 4B from well 4. A constant supply of magnesium ions, another important factor in dolomitiza- tion, was available to well 4 from the seawater entering the aquifer; therefore, the groundwater in the region of well 4 had the potential for dolomitization. However, any precipitation of dolomite would decrease the concentrations of calcium, magnesium, and bicarbonate ions in the groundwater. Such decreases were not evident in well 4, as shown by Figures 12, 13, and 15. There- fore, dolomitization may be kinetically inhibited, and the dolomite present in the aquifer matrix was probably the result of

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previous dolomitization.

Two (3 & 6) of the three wells (3, 4, & 6) within the region of the Pliocene-Miocene mixing zone were supersaturated with respect to calcite, aragonite, and dolomite. Well 4 was supersaturated with respect to dolomite, in equilibrium with calcite (S.I. = -0.004), and undersaturated with respect to aragonite. Supersaturation should indicate precipitation rather than dissolution; however, kinetic barriers exist that prevent the precipitation of calcite and dolomite. Before calcite or dolomite can precipitate, these barriers must be overcome. Kinetic studies have shown that concentrations as high as ten times the equilibrium calcite-solubility value are necessary for the nucleation and growth of calcite (Reddy, 1983). Also, the presence of phosphate, that was present in the aquifer matrix, and magnesium, from the seawater component, can inhibit precipitation by adsorbing to the calcite crystal and blocking a growth site (Morse, 1983). The low pH (7.04 to 7.43) of the groundwater indicated that the carbonate-ion concentration may be insufficient to break the magnesium dehydration barrier (Hanshaw and Back, 1979). It is possible that the relatively high groundwater-flow velocity in the regions of wells 3 and 6 kinetically inhibited the precipitation of calcite and dolomite even though the groundwater was supersaturated with respect to these minerals. Any precipitation of calcite and dolomite within the seawater region of the mixing zone represented by wells 3, 4, and 6 would decrease the concentrations of calcium, magnesium and bicarbonate

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ions. However, these decreases in concentration were not evident in these wells, as evidenced by Figures 12, 13, and 15. Therefore, the precipitation of calcite and dolomite was kinetically inhibited, and probably did not occur within the seawater region of the zone of dispersion of the Pliocene-Miocene aquifer.

A plot of the saturation indicies of calcite and dolomite versus the chloride concentrations of the groundwater samples (Figure 16) did not show any relationship between the depth, location, or seawater content and the saturation indicies. A conceptual model of the mixing zone in the Pliocene-Miocene aquifer of Cumberland Island was derived based on the available data. It can be assumed that a dilute, fresh, calcium-bicarbonate type groundwater flows through the aquifer under mainland Georgia toward Cumberland Island. This freshwater was probably very similar, or identical, to the composition of well 9. That freshwater mixed with seawater near the fringes of the island within the confined Pliocene-Miocene and Miocene Sand aquifers. The cyclical movement of the freshwater-saltwater interface caused by the tidal influence and dispersion had created zones of dispersion within the respective aquifers. The high pCO_2, low pH, low temperature, and high ionic strength of the mixed water caused the dissolution of $CaCO_3$ and the groundwater became oversaturated with respect to calcite and dolomite within the mixing zone, thereby producing high concentrations of calcium and bicarbonate ions within the mixing-zone waters. However, the carbonates were probably not precipitating because of kinetic

Figure 16

Comparison of S.I. vs. Cl concentration in mixing zone wells
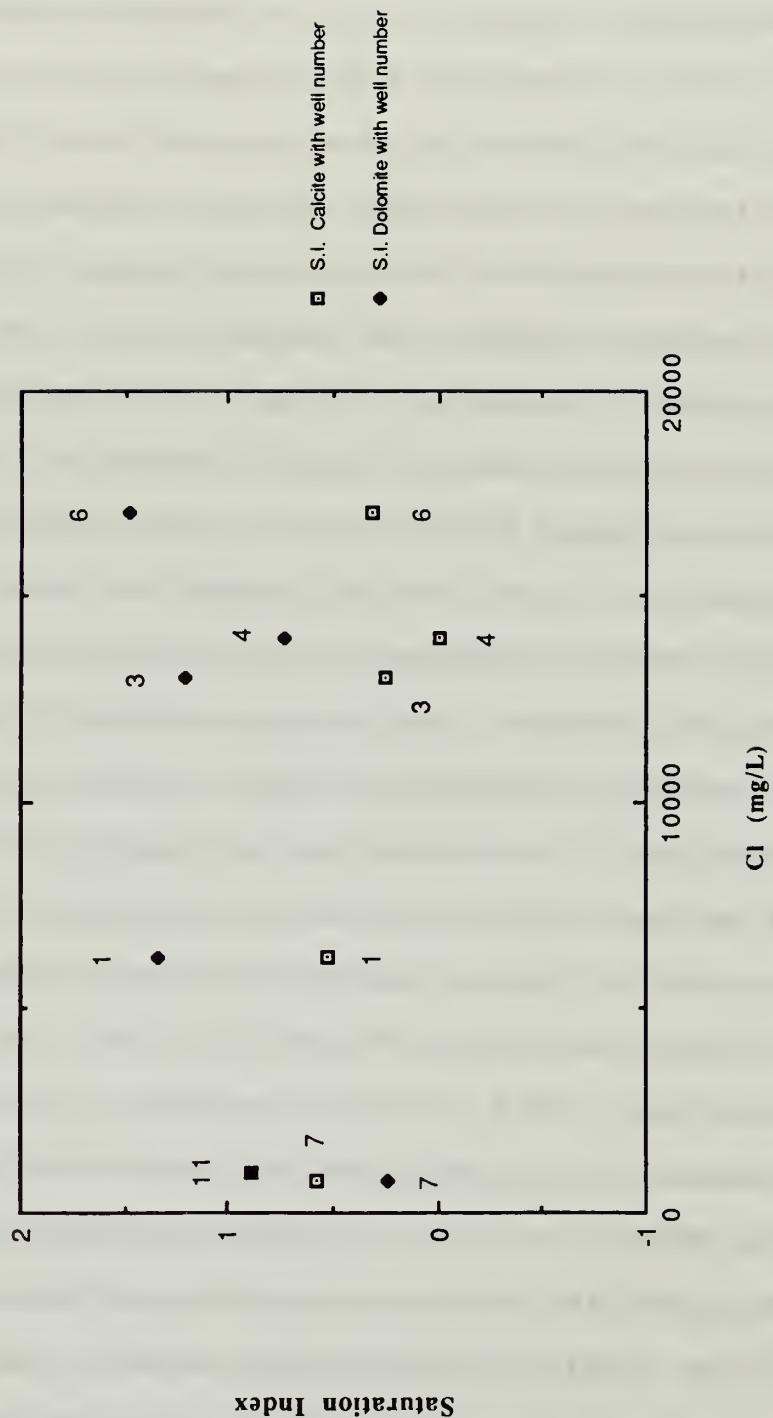
barriers. Sulfate reduction occurred in anaerobic zones along the flow path and within the mixing zone. Sulfate reduction was responsible for the lower-than-predicted sulfate concentrations and was partially responsible for the high bicarbonate concentrations observed in the mixing-zone wells.

Mixing-zone wells 3, 4, and 6 (as well as 1, 7, & 11) had a higher pCO_2 than either seawater or the probable freshwater-end member; therefore, the pCO_2 must have been generated by the oxidation of organic carbon. The seawater-end member was probably the source of the majority of the oxygen in the mixing zone. Once the oxygen was in the mixing zone, it oxidized organic carbon and produces CO_2. In wells 1 and 3, the groundwater was anoxic probably as the result of oxidation of organic matter.

Freshwater-Saltwater Interface in the Pliocene-Miocene Aquifer

The Pliocene-Miocene aquifer extends eastward from the mainland (where it is recharged), underneath the channel, to the island. From the island, it continues eastward underneath the ocean. Somewhere offshore of Cumberland Island the aquifer is directly exposed to seawater. Whether this exposure to seawater is natural or induced has not been determined. The possible reasons for exposure include a sudden change in slope in the ocean floor, or the shipping channel that was dredged immediately south and west of Cumberland Island. The channel was dredged to a total depth of 51 feet (15.5 m) below sea level, which may have penetrated the upper confining bed and exposed the underlying

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confined Pliocene-Miocene aquifer to seawater. Also, the U.S. Army Corps of Engineers drilled approximately 500 test holes in the channel area before the dredging began, and these may have also exposed the underlying Pliocene-Miocene aquifer to seawater. Because the test holes were drilled with seawater as the hydraulic fluid, any penetration into a confined aquifer would probably contaminate it with seawater.

Groundwater samples from the Pliocene-Miocene aquifer at sites 1, 2, and 3 (wells 3, 4, & 7, respectively) were dated by measuring the carbon-14 activity of the dissolved inorganic carbon. The dates obtained represent the apparent ages, and are not corrected for $CaCO_3$ dissolution. This dissolution, which is apparently occurring in the aquifer, would probably provide a source of nonradiogenic carbon, thereby increasing the apparent age of the water. The apparent ages were plotted versus the percentage of seawater present in each well (Figure 17). The results indicate that a fresh, carbonate groundwater about 8,000 years old is mixing with modern seawater in the Pliocene-Miocene aquifer. The graph illustrates that greater percentages of seawater in the mixed groundwater result in younger age dates. This occurs because the carbon-14 concentration of the old groundwater is diluted by the modern seawater. This confirms that well 7 and by implication well 11 are located within the zone of dispersion in the Pliocene-Miocene aquifer.

FIGURE 17

Graph of Apparent C14 age dates vs. seawater percentage

linear regression between age dates

$y = 82.757 - .010450x$ $R^2 = 0.985$

Apparent C14 Ages

Seawater Percentage in Wells

+   Well Number

with error bars
for age dates
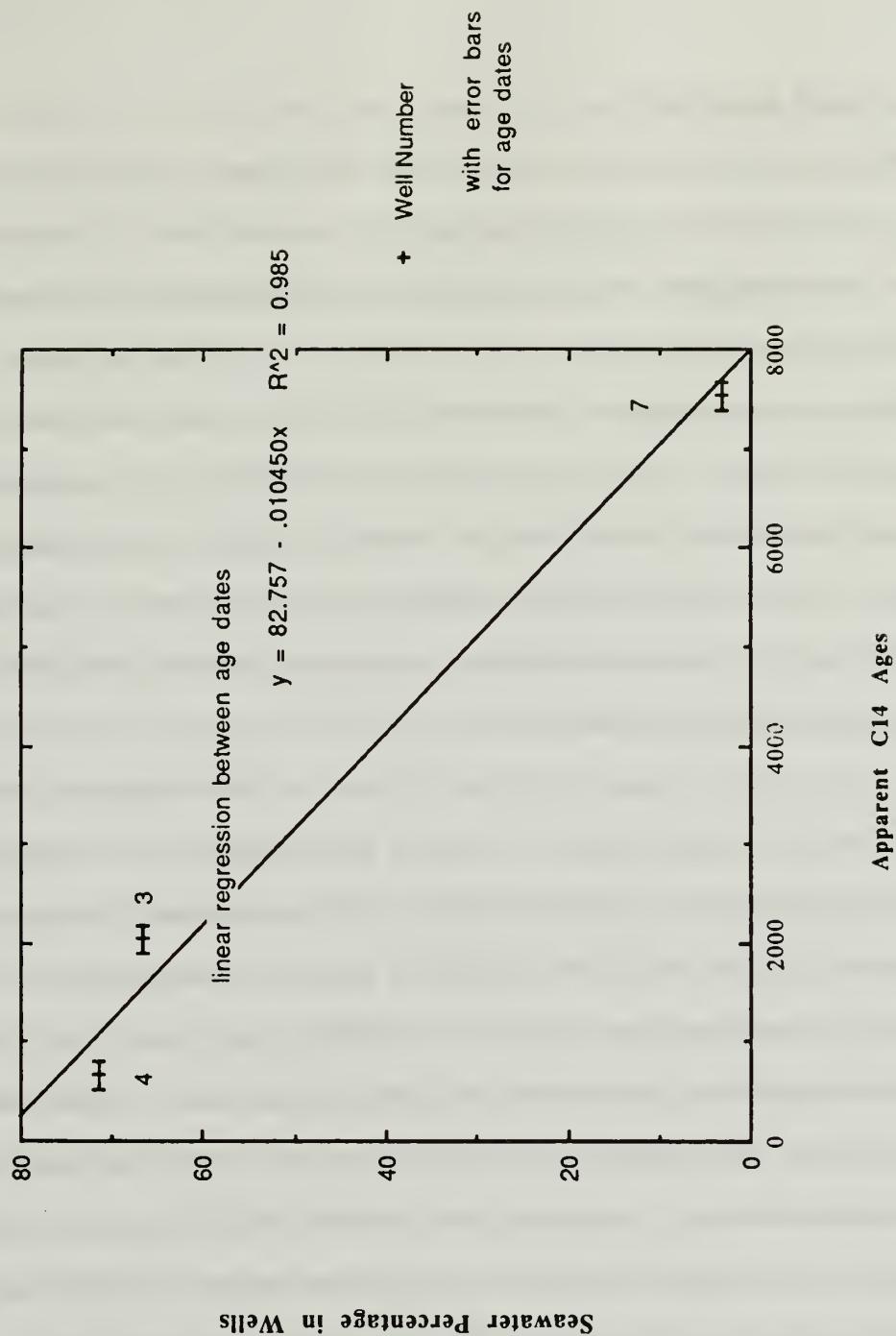
Miocene Sand Aquifer

The Miocene sand aquifers of the Charlton and Hawthorn Formations are located stratigraphically beneath the Pliocene-Miocene aquifer, and extend to the upper confining unit of the Floridan aquifer system (Clarke et al., 1990). In the Charlton, the aquifers are composed of sand layers that are confined by argillaceous dolomite. Only one Miocene sand aquifer located in the Charlton Formation, was sampled during this investigation (at well 1). This Miocene sand aquifer is composed of coarse-grained carbonate sand that is confined by overlying and underlying argillaceous dolomite units.

Well 1 at site 1 was drilled within a Miocene sand aquifer from 136 to 146 feet (41.5 to 44.5 m) (Figure 3). The groundwater in that well was approximately 32% seawater. This implies that the well was drilled within a zone of dispersion. Wells 1 and 3 are in a cluster, and well 1 (146 feet [44.5 m] deep) had a much lower seawater percentage (32%) than well 3 (94 feet [28.7 m] deep) with 67% seawater. This implies that the confining bed between wells 1 and 3 effectively separated these two aquifers into two flow regimes with two separate zones of diffusion. This also indicates that the zone of dispersion in the 79- to 94-foot (24.1- to 28.7-m) aquifer had intruded farther inland on the island than the zone of dispersion in the 136- to 146-foot (41.5- to 44.5-m) aquifer (Figure 3). This conclusion implies that the 79- to 94-foot (24.1- to 28.7-m) aquifer (well 3) had a higher hydraulic conductivity than the 136- to 146-foot (41.5- to 44.5-

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m) aquifer (well 1), or that the seawater head in the 79- to 94-foot (24.1- to 28.7 -) aquifer was higher, or that the freshwater head in the 79- to 94-foot (24.1- to 28.7-m) zone is lower. Any of these possibilities would cause the deeper intrusion of seawater into the island in the 79- to 94-foot (24.1- to 28.7-m) aquifer. A higher seawater head, however, might be caused by greater exposure of the aquifer tapped by well 3 to the ocean, indicating that somewhere offshore of Cumberland Island the 79- to 94-foot (24.1- to 28.7-m) aquifer was more exposed to seawater intrusion than the deeper aquifer. This exposure may be the result of the dredging or drilling previously mentioned, or it may be a natural exposure.

It is important to note that seawater intrusion occurred in both the Miocene-Pliocene (61 to 94 feet [18.6 to 28.7 m]) and Miocene sand aquifers (136 to 146 feet [41.4 to 44.5 m]) along the coast of the island. Although the navigation channel off-shore of Cumberland Island may be partially or wholly responsible for the saltwater intrusion in the Miocene-Pliocene aquifer, it cannot be the cause of the seawater intrusion in the deeper Miocene sand aquifer because of the confining bed that hydrologi-cally separates the two aquifers. Therefore, some other cause must exist for the seawater intrusion into the Miocene sand aquifer at site 1 (well 1). It is possible that the intrusion was caused by seawater entering the aquifer through a natural exposure of the Miocene sand aquifer offshore of Cumberland Island. It is also possible that the same factors that were the

cause the seawater intrusion into the Miocene sand aquifer were
also the cause of the seawater intrusion into the Pliocene-Mioc-
ene aquifer.

Well 1 was drilled into the mixing zone of a Miocene sand
aquifer. The Miocene sand aquifers were not monitored at site 3;
therefore, a possible freshwater-end member was not determined;
however, the freshwater-end member was probably a dilute, carbon-
ate groundwater.

Geochemistry: Previous Work

Information on the geochemistry of the Miocene sand aquifers
is limited. In the coastal Georgia area, most wells tap either
deeper or shallower water-bearing zones. Those wells that do tap
this zone tend to tap several of the aquifers. This makes
reliable water-quality data difficult to obtain.

A well near St. Marys, GA (across the St. Mary's River from
Cumberland Island), in the limestone unit 87 to 111 feet (26.5 to
33.8 m) below land surface yielded the values shown in Appendix
II (Westinghouse Environmental Services, 1989). This unit is
interpreted to be the same Miocene limestone-dolomite unit that
was encountered on Cumberland Island at 82 feet (25 m).

When the well was drilled deeper into the Miocene aquifer
system and screened from 344 to 502 feet (104.9 to 153.0 m), the
water quality results were notably similar to those of the 87- to
111-foot (26.5- to 33.8-m) zone (Appendix II) (Westinghouse,
1989). This well screened Miocene sand aquifers as reported by

McLemore et al. (1981), and the upper and lower Brunswick aquifers as reported by Clarke et al. (1990).

Geochemistry of the Miocene Sand Aquifer

The groundwater in the mixing zone of the Miocene sand aquifer in the region of well 1 was a sodium-chloride water type (Table 2). The chloride concentration (Cl = 6200 mg/L) from well 1 indicated a groundwater composition of about 32% seawater (Table 1). The groundwater appeared to be the result of simple two-end-member mixing of a dilute, carbonate water with seawater (Figures 10, 11, & 15). The figures show a "straight-line" dilution of seawater; however, the concentrations of calcium and bicarbonate ions were significantly greater than simple mixing would indicate (Figures 12 & 13). Also, the sulfate concentration was lower than simple mixing would indicate (Figure 14). Therefore, processes other than simple mixing must have had an effect on the composition of the mixed water.

The groundwater in well 1 was anaerobic (DO = 0.0 mg/L); therefore, sulfate reduction would explain the lower-than-expected sulfate concentrations. Sulfate reduction also produces bicarbonate ions as a by-product, which would contribute to the higher-than-predicted bicarbonate-ion concentration.

The high concentrations of calcium and bicarbonate ions were the result of the dissolution of the carbonate sand that comprises the aquifer matrix. A situation similar to that previously described for the mixing zone of the Pliocene-Miocene aquifer

existed in the Miocene sand aquifer at well 1. The mixture of a dilute, carbonate groundwater and seawater created a mixed water of high pCO_2 (log pCO_2 = -2.15), relatively low pH (7.43), low temperature (22.8°C), and high ionic strength (0.220) that was undersaturated with respect to calcite and aragonite. An apparently high groundwater velocity in this aquifer combined with the other factors to dissolve enough of the calcium-carbonate aquifer matrix for the solution to become supersaturated with respect to calcite and aragonite. The flow velocity was also apparently high enough that the solution circulated through the mixing zone and discharged into the ocean before re-equilibration with respect to calcite and aragonite occurs. Therefore, calcite and aragonite were kinetically inhibited from precipitation despite the supersaturation of the mixed water with respect to these minerals.

Summary of the Confined Aquifers

Rainwater that is very undersaturated with respect to all minerals falls on the recharge zone for the Pliocene-Miocene and Miocene sand aquifers of Cumberland Island. These areas are presumed to be in the coastal plain of mainland Georgia and of similar lithologic composition as the respective aquifers. The Pliocene-Miocene aquifer is composed of Pliocene carbonate sand and Miocene dolomite. The Miocene sand aquifers are composed of Miocene carbonate sand. As the rainwater enters the soil zone, CO_2 gas from the soil zone becomes dissolved in the water, and

the pCO_2 of the water increases. Because of the undersaturation of the water with respect to carbonate minerals and the high pCO_2 of the water, the rainwater begins to dissolve the calcite and dolomite matrix of the aquifers as it enters the saturated zone. This dissolution increases the concentrations of calcium, magnesium, and bicarbonate ions in the water. The regional hydraulic gradients in the aquifers of the Georgia coastal plain slope to the southeast, toward Cumberland Island. Eventually, the groundwater (flowing within confined aquifers) flows from mainland Georgia, underneath the St. Mary's River (which separates Cumberland Island from mainland Georgia), to Cumberland Island. When the carbonate groundwater reaches the seaward side of the island it mixes with seawater that has intruded into the aquifers. As previously discussed, the mixing of freshwater from the Pliocene-Miocene and Miocene sand aquifers with seawater has created zones of diffusion within the respective aquifers. The extent of the seawater intrusion is different in each of the two aquifers, and is dependent on factors such as freshwater head, hydraulic conductivity, and diffusion coefficient that were discussed previously.

The composition of the fresh, carbonate groundwater before it mixed with seawater was probably very similar in both aquifers. Both aquifers probably contained calcium-bicarbonate type water similar to that of well 9 (Table 1). When the freshwater mixed with the seawater, the composition obviously changed drastically. The composition of the water in the mixing zones was a function

of several factors, such as the percentages of freshwater and seawater in the mixture, the saturation indices of the minerals present within the aquifer matrix, the kinetics of the precipitation or dissolution of minerals, the pCO_2, the pH, and other factors previously discussed. The mixing of freshwater from the Pliocene-Miocene aquifer with seawater resulted in the mixtures found in wells 3, 4, and 6 (Table 1). The variations in composition of these wells was mainly caused by the variations in the percentage of seawater present.

FUTURE RESEARCH

The possibilities for future research on the geochemistry of the aquifers of Cumberland Island are numerous. A few suggestions are provided below.

1) Future analyses of the geochemistry of the groundwater and wells examined in this paper to determine if the freshwater-saltwater interfaces have moved landward or seaward with time.

2) Comparisons of the geochemistry of the coastal mixing zone wells (1, 3, 4, & 6) at high and low tides to determine to what extent the freshwater-saltwater interfaces move with the tide in their respective zones of diffusion.

3) A more comprehensive study of the geochemistry of the surficial aquifer using a series of 2-inch (5-cm) monitoring wells that could be hand-augered in place.

4) A comparison of the geochemistry of the Pliocene-Miocene aquifer and Miocene sand aquifer wells on the Georgia mainland in

Camden County with the equivalent wells on Cumberland Island.

CONCLUSIONS

1) Groundwater from well 1, in the zone of dispersion in the Miocene sand aquifer, was composed of a sodium-chloride water type. The groundwater in wells 3, 4, and 6, located in the zone of dispersion of the Pliocene-Miocene aquifer, also contained a sodium-chloride water type. Groundwater samples from wells 7 and 11 in the Pliocene-Miocene aquifer were a calcium-chloride water type. Groundwater from wells 9 and 10 that were located in the Pliocene sand unit and the lower confining bed of the Pliocene-Miocene aquifer, respectively, were a calcium-bicarbonate water type. Groundwater from well 2, located in the surficial aquifer, was also a calcium-bicarbonate water type. Groundwater from wells 5 and 8, also in the surficial aquifer, was a sodium-chloride type water.

2) Results of the analyses of the groundwater from the surficial aquifer indicated that the water quality varies considerably with geographic location. This resulted at least partially from the variation in rainfall or recharge over the island. For example, one well was located on a beach, another was located in a saltmarsh, and the third was located in a open forest area at Dungeness. The water quality of the surficial aquifer appeared to be susceptible to seasonal changes (as seen in well 2), as well as to contamination from salt spray or other sources. Well 8 at

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site 3 contained enough chloride concentration to suspect that saltspray was contributing to the groundwater recharge at this site.

3) The freshwater-saltwater interface was not encountered in the surficial monitoring wells; therefore, the interface must be further seaward of the monitoring wells.

4) A freshwater-saltwater zone of diffusion existed in the Pliocene-Miocene aquifer between 61 and 94 feet (18.6 and 28.7 m) below land surface. Very small percentages of saltwater were found to be mixing with freshwater in the dolomite unit of the Pliocene-Miocene aquifer at Dungeness, which is several hundred yards inland from the ocean. This was interpreted to be the freshwater region of the zone of diffusion. High percentages of saltwater were encountered in the Pliocene-Miocene aquifer wells at sites 1 and 2 along the southern coast of the island. These were interpreted to be the seawater region of the zone of diffusion.

5) The age dating of the Pliocene-Miocene groundwater indicated that the seawater intruding into the aquifer was modern. The age dates were consistent with the mixing model posed in this study.

6) The geochemistry of the seawater region of the zone of diffusion in the Pliocene-Miocene aquifer (wells 3, 4, & 6) was

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characterized by saltwater-freshwater mixing, calcite dissolu-
tion, and sulfate reduction. The calcite dissolution was driven
by the very high CO_2 content, low pH, low temperature, and high
ionic strength of the groundwater. That dissolution resulted in
very high concentrations of calcium and bicarbonate ions.
Sulfate reduction, which depleted the sulfate in the groundwater,
occurred in the anaerobic zones of the aquifers.

7)   The fresher regions of the zone of diffusion in the Pliocene-
-Miocene aquifer (wells 7 & 11) were characterized by freshwater-
-saltwater mixing, calcite dissolution, and reverse-ion exchange.

8)   Seawater has intruded the higher hydraulic conductivity unit
(well 6) of the Pliocene-Miocene aquifer at site 2 to a greater
extent than in the lower hydraulic conductivity unit (well 4).

9)   The seawater intrusion indicated that the Pliocene-Miocene
aquifer must be exposed to seawater somewhere offshore of Cumber-
land Island. The seawater intrusion may have resulted from the
dredging of the navigation channel, natural exposure, or some
combination of the two.

10)   Seawater intrusion existed within the confined Miocene
carbonate sand aquifer (well 1) also, but it was substantially
less than the Pliocene-Miocene aquifer stratigraphically above
it.

11) The seawater intrusion in the Miocene sand aquifer was probably the result of natural exposure of the aquifer to seawater. The navigation channel is not deep enough to penetrate the upper confining bed of this aquifer. Saltwater intrusion in the Miocene sand aquifer may have important implications for the source of saltwater in the overlying aquifer.

12) For the limestone-dolomite unit of the Pliocene-Miocene aquifer to have greater seawater intrusion than the surficial aquifer above it or the Miocene aquifer beneath it, it must be more exposed to seawater, or it must have a higher permeability than the other aquifers.

13) All of the mixing-zone waters (wells 1, 3, 4, & 6) were supersaturated with respect to dolomite, and all except well 4 were supersaturated with respect to calcite. Well 4 was in thermodynamic equilibrium with respect to calcite. Kinetic barriers prevented the precipitation of calcite and dolomite as evidenced by no decreases in concentrations of calcium, magnesium, and bicarbonate ions associated with precipitation.

14) No relationship existed between the saturation indicies of calcite and dolomite, and the location, depth, or seawater content of the groundwater of Cumberland Island.

15) The mixing that occurred in wells 1, 3, 4, and 6 was mixing

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of two-end members: dilute, carbonate groundwater and seawater. The concentrations of magnesium, sodium, potassium, and chloride ions in these wells were "straight-line dilutions" of seawater. The sulfate concentrations were lower than predicted by simple mixing because of sulfate reduction. Sulfate reduction also contributed to the higher-than-simple-mixing concentrations of bicarbonate. The concentrations of calcium and bicarbonate ions were higher than simple mixing because of calcium carbonate dissolution.

16) The Pliocene-Miocene aquifer (61- to 94-foot [18.6- to 28.7-m] zone) was heterogeneous composed of variable hydraulic conductivity zones that can be either aerobic or anaerobic.

17) The dolomite present in the Pliocene-Miocene aquifer was probably formed prior to present day. Calcium carbonate appeared to be dissolving in this aquifer, but dolomite did not appear to be precipitating or replacing the calcium carbonate.

REFERENCES

American Public Health Association (APHA). 1985. <u>Standard methods for the examination of water and wastewater</u>. 16 th Ed. APHA, Washington, D. C. 1268 pp.

Appelo, C. A. G., & A. Willemsen. 1987. Geochemical calculations and observations on saltwater intrusions, I. a combined geochemical/mixing cell model. J. Hydrol. 94:313--330.

Back, W., & B. B. Hanshaw. 1970. Comparison of chemical hydrogeology of the Carbonate Peninsulas of Florida and Yucatan. J. Hydrol. 10:330-368.

Badiozamani, K. 1973. The Dorag Dolomitization Model - Application to the Middle Ordovician of Wisconsin. J. Sed. Petrol. 43:965-984.

Bolin, B. 1974. The Carbon Cycle. <u>in</u>. <u>Planet Earth-Readings from Scientific American</u>. San Francisco, CA: W.H. Freeman Co.

Boylan, D. 1986. The hydrogeologic resources of North Padre Island; Coastal South Texas. M. S. Thesis, Baylor University, Waco, Texas.

Brown, D. P. 1984. Impact of development on availability and quality of groundwater in Eastern Nassau County, Florida, and Southeastern Camden County, Georgia. U. S. Geological Survey Water-Resources Investigations Report 83-4190. 113 pp.

Busenberg, E., & L. N. Plummer. 1986. A comparative study of the dissolution and crystal growth kinetics of Calcite and aragonite. <u>in</u>. F. A. Mumpton (ed.). <u>Studies in Diagenesis</u> U. S. G. S. Bull. 1578. pp. 139-168.

Clarke, J. S., C. M. Hacke, & M. F. Peck. 1990. Geology and groundwater resources of the coastal area of Georgia. Georgia Geologic Survey Bulletin 113. ???pp.

Cooper, H. H., Jr. 1959. A hypothesis concerning the dynamic ✳ balance of freshwater and saltwater in a coastal aquifer. J. Geophysical Res. 64(4):461-467.

Drever, J. I. 1988. <u>The Geochemistry of Natural Waters</u>. 2nd Ed. Prentice-Hall, Englewood Cliffs, NJ. 388 pp.

Fetter, C. W. 1972. Position of the Saline Water Interface ✳

beneath oceanic islands.   Water Resources Res.   3(5):1307--
1315.

Freeze, R. A., & J. A. Cherry.   1979.   <u>Groundwater</u>. Prentice-
-Hall, Englewood Cliffs, NJ.   604 pp.

Folk, R. L., & L. S. Land.   1975.   Mg/Ca ratio and salinity:
Two controls over crystallization of dolomite.   Am. Assoc.
Petrol. Geol. Bull. 59. pp. 60-68.

Grantham, R. G. & W. R. Stokes.   1976.   Groundwater quality
data for Georgia.   U. S. Geological Survey.   Water Resources
Division, Doraville, Ga., 216 pp.

Hanshaw, B. B., W. Back, & R. G. Deike.   1971.   A geochemical
hypothesis for Dolomitization by groundwater.   Econ. Geolo-
gy.   66:710-724.

Hanshaw, B. B., & W. Back.   1979.   Major geochemical processes
in the evolution of Carbonate-Aquifer Systems.   J. Hydrol.
43:287-312.

Hardie, L. A.   1987.   Dolomitization: A critical view of some
current views.   J. Sed. Petrol.   57:166-183.

Harris, W. H.   1967.   Stratification of fresh- and saltwater
on barrier islands as a result of differences in sediment
permeability.   Water Resources Res.   3(1):89-97.

Leve, G. W.   1966.   Groundwater in Duval and Nassau Counties,
Florida.   Florida Geol. Surv. Report of Investigations No.
43.   91 pp.

Longman, M. W.   1982.   Carbonate Diagenesis as a control on
stratigraphic traps (with examples from the Williston Ba-
sin).   AAPG Education Course Note Series #21.   American
Assoc. Petrol. Geologists, Tulsa, OK.   159 pp.

McCallie, S. W.   1898.   Preliminary report on the Artesian
Well System of Georgia.   Georgia Geol. Surv. Bull. No. 7.
pp. 74-84.

McLemore, W. H., C. E. Swann, P. B. Wigley, M. C. Turlington,
V. J. Henry, J. Martinez, R. E. Carver, & J. T. Thurmond.
1981.   Geology as applied to land-use management on Cumberl-
and Island, Georgia. Georgia Geologic Survey, Atlanta, Ga.

Morse, J. W.   1983.   The kinetics of calcium carbonate disso-
lution and precipitation.   <u>in</u>.   R. J. Reeder (ed.).   <u>Carbon-
ates: Mineralogy and Chemistry, Reviews in Mineralogy</u>.
11:227-264.   Mineralogical Society of America, Washington,
D. C.

Motz, L. H. 1982. Lower Hawthorn Aquifer on Sanibel Island,
    Florida. Ground Water. 20(2):170-178.

Nadler, A., M. Margaritz, & E. Mazor. 1980. Chemical reac-
    tions of seawater with rocks and freshwater: Experimental
    and field observations on brackish waters in Israel. Geoch-
    em. Cosmo Acta. 44:879-886.

Nordstrom, D. k., L. N. Plummer, T. M. L. Wigley, T. J. Wole-
    ry, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerat, T.
    M. Florence, B. Fritz, M. Hoffman, G. R., Jr. Holdren, G. M.
    Lafon, S. V. Mattigod, R. E. McDuff, F. Morel, M. M. Reddy,
    G. Sposito, & J. Thrailkill. 1979. A comparison of comput-
    erized chemical models for equilibrium calculations in
    aqueous systems. in. E. A. Jenne (ed.). Chemical Modeling
    in Aqueous Systems, Speciation, Sorption, Solubility, and
    Kinetics. Series 93. American Chemical Society. pp.
    857-892.

Plummer, L. N. 1975. Mixing of seawater with calcium carbon-
    ate groundwater. in. E. H. T. Whitten (ed.). Quantitative
    Studies in the Geological Sciences. Geol. Soc. Am. Mem.
    142:219-236.

Plummer, L. M. 1977. Defining reactions and mass transfer in
    part of the Floridan Aquifer. Water Resour. Res. 13:801--
    812.

Plummer, L. N., B. F. Jones, & A. H. Truesdell. 1976. WATEQF -
A FORTRAN IV Version of WATEQ, A computer program for calculating
chemical equilibrium of natural waters, User's Guide. U. S.
Geol. Surv. Water-Resources Investigation. pp. 13-76.

Randazzo, A. F., & J. I. Bloom. 1985. Mineralogical changes
    along the freshwater/saltwater interface of a modern aqui-
    fer. Sed. Geology. 43:219-239.

Reddy, M. M. 1983. Characterization of calcite dissolution
    and precipitation using an improved experimental technique.
    Sci. Geol. Mem. 71:109-117.

Runnels, D. D. 1969. Diagenesis, chemical sediments, and the
    mixing of natural waters. J. Sed. Petrol. 39:1188-1201.

Sanford, W. E., & L. F. Konikow. 1989a. Porosity development
    in coastal carbonate aquifers. Geology. 17:249-252.

Sanford, W. E., & L. F. Konikow. 1989b. Simulation of cal-
    cite dissolution and porosity changes in saltwater mixing
    zones in coastal aquifers. Water Resources Res. 25(4):655-
    -667.

Stewart, M. T. 1982. Evaluation of electromagnetic methods for rapid mapping of saltwater interfaces in coastal aquifers. Ground Water. 20(5):??-??.

Stoessell, R. K., W. C. Ward, B. H. Ford, & J. D. Schuffert. 1989. Water chemistry and CaCO3 dissolution in the saline part of an Open-Flow Mixing Zone, Coastal Yucatan Peninsula, Mexico. Geol. Soc. Am. Bull. 101:159-169.

Stringfield, V. T. 1966. Artesian water in tertiary limestone in the southeastern States. U. S. Geol. Surv. Professional Paper 517. 226 pp.

Trainer, F. W., & R. C. Heath. 1976. Bicarbonate content of groundwater in carbonate rock in Eastern North America. J. Hydrol. 31:37-55.

Vacher, H. L. 1988a. Dupuit-Ghyben-Herzberg analysis of strip-island lenses. Geological Society of America Bulletin. 100:580-591.

Vacher, H. L. 1988b. Groundwater in barrier islands - theoretical analysis and evaluation of the unequal-sea level problem. J. Coastal Res. 4(1):139-148.

Volker, R. E., & K. R. Rushton. 1982. An assessment of the importance of some parameters for seawater intrusion in aquifers and a comparison of dispersive and Sharp-Interface Modelling approaches. J. Hydrol. 56:239-250.

Warren, M. A. 1944. Artesian water in Southeastern Georgia, with special references to the coastal area. Georgia Geologic Surv. Bull. Vol. 49. 140 pp., and 49-A, "Well Records", 83 p.

Warren, M. A. 1944. Well records. Georgia Geologic Serv. Bull. Vol. 49-A. 83 pp.

Westinghouse Environmental Services. 1989. Ground water availability at the Osprey Cove Subdivision, Camden County, Georgia. Report No. 1171-89-223.

Wigley, T. M. C., & L. N. Plummer. 1976. Mixing of carbonate waters. Geochem. Cosmo. Acta. 40:989-995.

APPENDIX I

GEOCHEMICAL DATA FROM PREVIOUS INVESTIGATIONS

Data from Clarke et al. (1990) for five surficial aquifer wells
in mainland Camden County, GA, at depths of 12 to 18 feet (3.7 to
5.5 m).

Sulfate: <5 - 166 mg/L   Hardness (as $CaCO_3$): 16 - 304 mg/L

Iron: 1.65 - 4.98 mg/L   Fluoride: <0.01 - 0.54 mg/L

pH: 4.0 - 6.6   Chloride: 10.3 - 42.8 mg/L

Specific conductance: 132 - 740 micromhos per cm at 25 C

TDS as residue at 180 C: 71 - 474 mg/L

The chemical constituents of the Pliocene-Miocene aquifer of
Cumberland Island analyzed by McLemore et al. (1981).

Chloride: 50.0 ppm   pH: 7.65

Silica: 20.3 ppm   Fluoride: 0.16 ppm

Iron: 0.24 ppm   Nitrate (NO_3): 0 ppm

Manganese: 0 ppm   Phosphate (PO_4): 0 ppm

Calcium: 54.3 ppm   Sulfide (S): 15.3 ppm

Magnesium: 8.0 ppm   Bicarbonate (HCO_3): 170.6 ppm

Sodium: 22.0 ppm   Alkalinity ($CaCO_3$): 140.0 ppm

Potassium: 1.9 ppm   Hardness (as $CaCO_3$): 168.6 ppm

Sulfate: 6.5 ppm   TDS: 322.2 ppm

Data from a 87- to 111-foot (26.5- to 33.8-m) well in Miocene limestone unit near St. Marys, GA (Westinghouse, 1989).

Sodium: 23 mg/L   Specific Conductance: 448 umhos/cm

Magnesium: 19mg/L   Total Dissolved Solids: 388 mg/L

Calcium: 35 mg/L   Iron: <0.05 mg/L

Sulfate: 82 mg/L   Manganese: <0.05 mg/L

Chloride: 14 mg/L   Flouride: 0.4 mg/L

Bicarbonate: 180 mg/L

Data from a 344- to 502-foot (104.9- to 153.0-m) well in Miocene limestone unit near St. Marys, GA (Westinghouse, 1989).

Calcium: 41 mg/L   TDS: 556 mg/L

Magnesium: 34 mg/L   Iron: <0.05 mg/l

Sodium: 28 mg/L   Manganese: <0.05 mg/L

Sulfate: 155 mg/l   Flouride: 0.6 mg/L

Chloride: 23 mg/l   Bicarbonate: 170 mg/L

As the nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for enjoyment of life through outdoor recreation. The department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people. The department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for American Indian reservation communities and for the people who live in island territories under U.S. administration.